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(54) Title: BASE OIL FOR WELL-BORE FLUIDS			
(57) Abstract A base oil for well-bore fluids, such as drilling fluids, comprising normal alkanes having from 11 to 16 carbon atoms, with no more than a trace of the normal alkanes having greater than 16 carbon atoms, and having a pour point at less than -2 °C, as well as low toxicity and good aerobic and anaerobic biodegradability.			
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Asserted Claim 114
(depends from Asserted Claim 3)

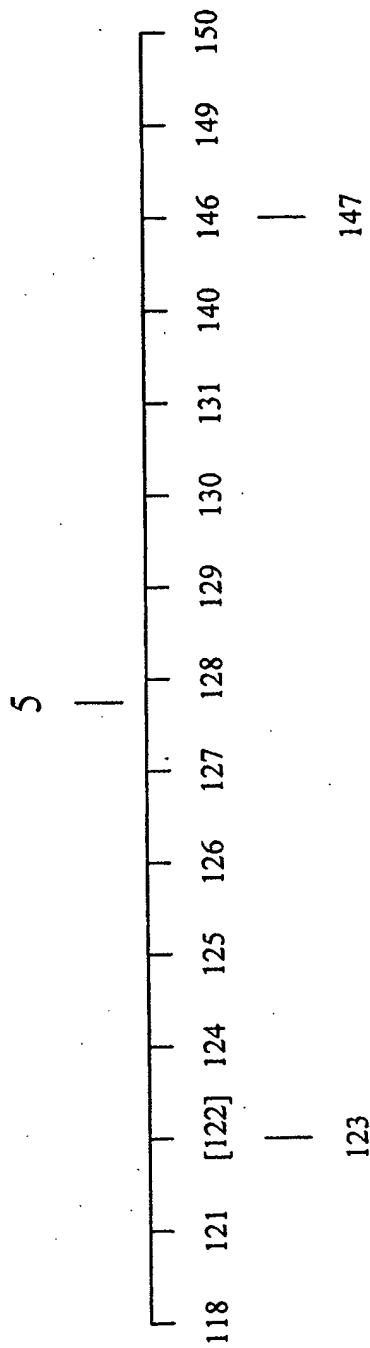
Element	References	Location of Element in Each Reference
114. The method of claim 3 wherein said drilling fluid comprises at least one additive selected from the group consisting of rheology control agents, viscosifiers, filtration control agents, and HTHP additives.	(A)	p. 1; See Reference (I) at 195
	(B)	Petrofree brochure p. 5 (table); RM-63 brochure p. 1
	(D)	col. 6 ll. 12-16
	(E)	col. 2 ll. 40-45; col. 3 ll. 42-46, 52-55
	(F)	col. 2 ll. 1-6; col. 12 ll. 60-62; col. 13 ll. 13-16
	(G)	p. 1 col. 2 to p. 2 col. 1
	(H)	p. 365 col. 1; p. 367 col. 1
	(M)	p. 3 col. 2; p. 4 col. 1
	(N)	p. 2 col. 2; p. 5 col. 2
	(O)	p. 1 col. 1; tables 9-10
	(P)	p. 4
	(Q)	HAL_0015055
	(R)	p. 1 ll. 27-30; p. 10 ll. 31-33
	(S)	p. 1 ll. 26-29; p. 12 ll. 29-31

Asserted Claim 117

(depends from Asserted Claim 3)

Element	References	Location of Element in Each Reference
117. The method of claim 3 wherein said drilling fluid forms a structure that is capable of suspending drill cuttings at rest and that is instantaneously disruptible by movement.	(A) (I) (Q)	p. 2 cols. 1-2; p. 2 col. 2 to p. 3 col. 1 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 5
& Dependent Asserted Claims



Asserted Claim 5

Element	References	Location of Element in Each Reference
5. A fragile gel drilling fluid comprising:		SEE ENDNOTE ²
(a) an invert emulsion base;	(A) (B) (D) (E) (F) (G) (J) (H) (K) (L) (M) (N) (O) (P) (Q) (R) (S)	Prior art drilling fluids combining elements (a) through (d) below — invert emulsion base, thinners, emulsifiers, and weighting agents — commonly were used in drilling operations before June of 2001, one year before the filing date of the '832 patent. (I) at pp. 21-22, 29, 109-110. p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1-2, 5 (table); RM-63 brochure pp. 1-2 col. 1 ll. 50-52; col. 6 ll. 12-19 abstract; col. 1 ll. 10-11, 34-40; col. 3 ll. 39-64; col. 8 ll. 15-63; col. 9 ll. 3-31 abstract; col. 1 ll. 37-49; col. 1 l. 62 to col. 2 l. 3; col. 3 ll. 38-50; col. 12 ll. 20-26; col. 14 ll. 63-68 pp. 1-2, 8-9 & table 1 p. 1 cols. 1-2; p. 3 col. 1; p. 4 col. 1 pp. 4-5, 13, 15-16 p. 363 col. 1; p. 364 col. 1; p. 368 col. 1 p. 1 cols. 1-2; p. 2 col. 2; p. 3 col. 1 p. 1 cols. 1-2; p. 2 col. 1; p. 4 col. L; table 5 p. 1 cols. 1-2; p. 2 col. 2 p. 1 cols. 1-2; tables 9-10 pp. 2, 5, 7 HAL 0015055, 0015102; See Reference (A) above p. 1 ll. 7-8, 22-26; p. 5 ll. 6-18; p. 7 l. 29 to p. 8 l. 26; p. 11 l. 30 to p. 12 l. 2 (table); p. 15 ll. 15-19 abstract; p. 1 ll. 7, 21-25; p. 5 l. 24 to p. 6 l. 4; p. 9 l. 19 to p. 10 l. 17; p. 16 ll. 16-35 (table)
(b) one or more thinners;	(A) (B) (C) (D) (E) (F) (G) (H) (I) (J) (K) (P)	p. 3 at cols. 1-2; Fig. 4; Figs. 13-14 col. 13 ll. 29-33; col. 15 ll. 5-6 Petrofree brochure p. 5 (table) col. 1 l. 28 to col. 2 l. 31 abstract; col. 2 ll. 52-50; col. 3 l. 7 to col. 4 l. 60; col. 5 ll. 48-57 p. 2 ll. 15, 26; p. 4 ll. 29-32; p. 9 table 1 p. 5 col. 1 p. 365 col. 1; p. 367 col. 1 pp. 195, 204 abstract; col. 3 ll. 47-49, 60-64; col. 4 ll. 18-30; col. 4 l. 58 to col. 5 l. 33; col. 6 ll. 19-29 pp. 18-19 p. 4

	(Q) (R) (S)	<p>HAL_0015067, 0015202-03; See Reference (A) above p. 1 ll. 7-10; p. 2 ll. 14-17; p. 4 ll. 1-10; p. 5 l. 19 to p. 6 l. 4; p. 6 l. 8 to p. 7 l. 4; p. 12 ll. 1-2 (table), 7-16; p. 15 ll. 21-24 abstract; p. 1 ll. 8-9; p. 2 ll. 14-17; p. 3 l. 16 to p. 4 l. 19; p. 6 ll. 5-30; p. 13 ll. 19-30; p. 14 ll. 3-31; p. 16 (table); p. 17 ll. 5-11</p>
(c) one or more emulsifiers; and	(A) (B) (D) (E) (F) (G) (H) (I) (K) (L) (M) (N) (O) (P) (Q)	<p>p. 1 cols. 1-2; p. 2 cols. 1-2 Petrofree brochure pp. 1, 5 (table) col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 9 ll. 50-63; col. 10 ll. 21-28 col. 2 ll. 1-4; col. 12 l. 60; col. 15 ll. 7-10 p. 1 col. 2; p. 3 col. 1 p. 365 col. 2; p. 366 col. 2 p. 1 l. 34; p. 2 ll. 11-12, 22-23; p. 7 ll. 22-35; p. 9 l. 3 & table 1 abstract; pp. 4-9 p. 3 col. 1 p. 3 cols. 1-2; p. 4 col. 1; p. 5 col. 1; figs. 3-4 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 5 col. 1 p. 2 col. 1; tables 9-10 pp. 4, 7 HAL_0015055 See Reference (A) above p. 1 ll. 27-29; p. 10 ll. 31-33; p. 12 ll. 1-2 (table) p. 1 ll. 26-28; p. 12 ll. 29-31; p. 16 (table)</p>
(d) one or more weighting agents,	(A) (B) (D) (E) (F) (G) (H) (J) (K) (L) (M) (N) (O) (P) (Q) (R)	<p>p. 1 col. 1; p. 2 col. 1 Petrofree brochure p. 5 (table); RM-63 brochure pp. 1-2 col. 6 ll. 12-19 abstract; col. 1 ll. 40-42; col. 3 ll. 43-46, 52-54; col. 10 ll. 8-15 col. 2 ll. 1-5; col. 13 ll. 9-12; col. 15 l. 11 p. 5 col. 2; p. 3 col. 1; p. 4 col. 2 p. 367 col. 2 p. 1 l. 35; p. 2 ll. 12, 23; p. 4 ll. 16-18; p. 8 ll. 1-3; p. 9 l. 8 & table 1 pp. 18, 21 p. 1 col. 2; p. 3 col. 1; p. 4 col. 1; p. 6 col. 1 fig. 9 & p. 4 cols. 1-2; fig. 15 & p. 5 col. 2; p. 6 col. 2 p. 1 cols. 1-2; p. 2 cols. 1-2; p. 4 col. 1 to p. 5 col. 1 p. 1 col. 1; p. 2 col. 1; tables 9-10 pp. 4, 7 HAL_0015055 See Reference (A) above p. 1 ll. 27-29; p. 2 ll. 10-11; p. 10 ll. 23-30; p. 12 ll. 1-2 (table)</p>

wherein said fluid is visco-elastic.	(S)	p. 1 ll. 26-28; p. 2 ll. 10-11; p. 12 ll. 20-28; p. 16 (table)	

Asserted Claim 118
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
<p>118. The drilling fluid of claim 5 wherein said invert emulsion has a continuous base comprised of at least one component selected from at least one of the following groups:</p> <p>(i) esters prepared from fatty acids and alcohols, esters prepared from olefins and fatty acids or alcohols;</p> <p>(ii) olefins comprising linear alpha olefins, isomerized olefins having a straight chain, olefins having a branched structure, isomerized olefins having a cyclic structure; olefin hydrocarbons;</p> <p>(iii) paraffin hydrocarbons comprising linear paraffins, branched paraffins, poly-branched paraffins, cyclic paraffins, isoparaffins;</p> <p>(iv) mineral oil hydrocarbons;</p> <p>(v) glyceride triesters comprising rapeseed oil, olive oil, canola oil, castor oil, coconut oil, corn oil, cottonseed oil, lard oil, linseed oil, neatsfoot oil, palm oil, peanut oil, perilla oil, rice bran oil, safflower oil, sardine oil, sesame oil, soybean oil, sunflower oil; and</p> <p>(vi) naphthenic hydrocarbons.</p>	<p>(A) (B) (F) (G) (J) (K) (P) (Q) (R) (S)</p>	<p>p. 1 cols. 1-2; p. 3 col. 1; tables 2-5; Fig. 16 col. 2 ll. 1-15 col. 1 ll. 41-49; col. 2 ll. 26-29, 36-46; col. 7 ll. 1-6, 39-48 p. 1 col. 2 p. 2 ll. 1, 3-4, 13-14, 25, 30; p. 3 ll. 8-9, 15-31; p. 4 ll. 1-15; p. 8 ll. 30-35; p. 9 table 1 pp. 13, 15-16 p. 2 HAL_0015053-54 See Reference (A) above p. 8 ll. 6-26; p. 9 ll. 5-22; p. 15 ll. 15-24 p. 9 l. 29 to p. 10 l. 17; p. 10 l. 29 to p. 11 l. 15</p>

Asserted Claim 121
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
121. The drilling fluid of claim 5 wherein said drilling fluid forms a structure that is capable of suspending drill cuttings at rest and that is instantaneously disruptible by movement.	(A) (I) (Q)	p. 2 cols. 1-2; p. 2 col. 2 to p. 3 col. 1 p. 39 ll. 3-7 See Reference (A) above

Asserted Claim 123
(depends from Asserted Claim 5 and Unasserted Claim 122)

Element	References	Location of Element in Each Reference
123. The drilling fluid of claim 122 wherein when used in drilling said fragile gel reverts to a flowable or liquid state immediately upon resumption of drilling after a period of rest.	(A) (Q)	p. 2 cols. 1-2; p. 3 col. 1 See Reference (A) above

Asserted Claim 124
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
124. The drilling fluid of claim 5 wherein the ECDs of said fluid when used in drilling boreholes are less than about 0.5.	(A) (Q)	Figs. 11-12; p. 3 col. 1; p. 4 col. 1 See Reference (A) above

Asserted Claim 125
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
125. The drilling fluid of claim 5 said drilling fluid is substantially free of organophilic clay.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55 See Reference (A) above p. 11 ll. 12-14

Asserted Claim 126
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
126. The drilling fluid of claim 5 wherein said fluid does not require organophilic clays to provide filtration control when used in drilling.	(B) (N) (O) (Q) (R)	Petrofree brochure p. 6; RM-63 brochure p. 1 p. 2 col. 2; p. 5 col. 2 p. 2 cols. 1-2; p. 3 col. 1; p. 9 HAL_0015053-55 See Reference (A) above p. 11 ll. 12-14

Asserted Claim 127
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
127. The drilling fluid of claim 5 wherein said fluid does not exhibit sag when at rest.	(B) (G) (L) (M)	RM-63 brochure p. 1 p. 4 col. 1 p. 1 col. 2; p. 3 col. 2; p. 6 cols. 1-2 p. 1 col. 1; p. 4 cols. 1-2; p. 5 col. 2; p. 6 cols. 1-2

Asserted Claim 128
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
128. The drilling fluid of claim 5 wherein said drilling fluid has at least one property selected from the group consisting of fragile gel behavior, no appreciable pressure spike upon resumed drilling, low difference in surface and downhole equivalent circulating densities, no significant sag, and generally flat rheology between higher and lower temperatures.	(A) (B) (E) (G) (L) (M) (N) (Q) (R) (S)	p. 2 col. 2 to p. 3 col. 1; p. 3 col. 1 & Figs. 11-12; p. 3 col. 1; p. 4 col. 1; Figs. 11-12 RM-63 brochure p. 1 col. 4 ll. 24-30 p. 4 col. 1; p. 1 col. 1; p. 2 col. 1; p. 6 p. 5 col. 2; p. 1 col. 2; p. 3 col. 2; p. 6 cols. 1-2; p. 1 col. 2; p. 3 col. 2 p. 1 col. 1; p. 4 cols. 1-2; p. 5 col. 2; p. 6 cols. 1-2 p. 1 col. 2; p. 6 col. 1 HAL_0015054; HAL_0015101-102; See Reference (A) above p. 3 ll. 24-33; p. 7 ll. 17-25; p. 14 (table 1a); p. 16 (tables 2-3); p. 17 (tables 4-5); p. 18 (table 7); p. 19 (table 8) p. 18 (table 1); p. 20 (table 3); p. 21 (table 5); p. 22 (tables 6-7); p. 23 (table 9); p. 24 (table 10); p. 25 (tables 12-13); p. 26 (tables 14-15)

Asserted Claim 129
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
129. The drilling fluid of claim 5 wherein said drilling fluid has a lower yield point at lower temperatures than at higher temperatures.	(R) (S)	p. 7 ll. 17-25; p. 17 (table 5) p. 18 (table 1)

Asserted Claim 130
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
130. The drilling fluid of claim 5 wherein said drilling fluid has a lower yield point at temperatures from about 40° F. to about 60° F. than at temperatures of about 120° F. or higher.	(R) (S)	p. 2 ll. 19-28; p. 3 ll. 19-21; p. 7 ll. 19-25; p. 14 (table 1) & pp. 16-19 (tables 2-9) p. 2 l. 30 to p. 3 l. 3; p. 17 ll. 23-26; pp. 18-27 (tables 1-17)

Asserted Claim 131
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
131. The drilling fluid of claim 5 wherein said fluid is tolerant to drill cuttings when used in drilling.	(A)	p. 1 cols. 1-2; p. 2 cols. 1-2; Figs. 4-6
	(I)	p. 30 l. 3 to p. 31 l. 8
	(L)	p. 1 col. 2
	(O)	p. 1 col. 1; p. 3 col. 1
	(P)	p. 1
	(Q)	HAL_0015055; See Reference (A) above
	(R)	p. 13 ll. 1-5; p. 14 (table 1); pp. 16-19 (tables 2, 4, 6, 9)

Asserted Claim 140
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
140. The drilling fluid of claim 5 wherein said drilling fluid is ester-free.	(A) (H) (M) (N)	Figs. 15-16; p. 1 col. 2; p. 2 col. 2 pp. 3-6 p. 1 col. 2 to p. 2 col. 1 p. 2 col. 2 to p. 3, col. 1, pp. 8-12

Asserted Claim 146
(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
146. The drilling fluid of claim 5 wherein said drilling fluid comprises at least one additive selected from the group consisting of rheology control agents, viscosifiers, filtration control agents, and HTHP additives.	(A)	p. 1; See Reference (I) at 195
	(B)	Petrofree brochure p. 5 (table); RM-63 brochure p. 1
	(D)	col. 6 ll. 12-16
	(E)	col. 2 ll. 40-45; col. 3 ll. 42-46, 52-55
	(F)	col. 2 ll. 1-6; col. 12 ll. 60-62; col. 13 ll. 13-16
	(G)	p. 1 col. 2 to p. 2 col. 1
	(H)	p. 365 col. 1; p. 367 col. 1
	(M)	p. 3 col. 2; p. 4 col. 1
	(N)	p. 2 col. 2; p. 5 col. 2
	(O)	p. 1 col. 1; tables 9-10
	(P)	p. 4
	(Q)	HAL_0015055
	(R)	p. 1 ll. 27-30; p. 10 ll. 31-33
	(S)	p. 1 ll. 26-29; p. 12 ll. 29-31

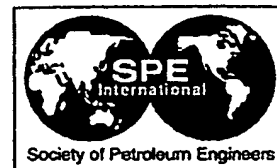
Asserted Claim 149

(depends from Asserted Claim 5)

Element	References	Location of Element in Each Reference
149. The fluid of claim 5 wherein said fluid is used in drilling a borehole in a subterranean formation such that there is a reduction in the loss of drilling fluid into said subterranean formation.	(A) (B) (J) (L) (N) (P)	p. 3 col. 1 RM-63 brochure p. 1; See Reference 1 pp. 42; 199-200 p. 2 ll. 23-24; p. 8 ll. 7-10 p. 3 at col. 2 ll. 23-26 p. 5 at col. 2 ll. 7-29 pp. 7, 12; See Reference 1 pp. 42; 199-200

¹ The preamble is not a claim element. Even if the preamble is a claim element, "fragile gel" characteristics and behaviors are inherent in the drilling fluids comprising elements (a) through (d) of each and every asserted claim. See, e.g., the following references:

- (A) p. 2 col. 1; p. 2 col. 2 to p. 3 col. 1; p. 3 cols. 1-2; p. 4 col. 1
- (B) RM-63 brochure p. 1
- (H) p. 365 col. 2; p. 366 col. 1; p. 367 col. 2; p. 368 col. 1
- (L) p. 1 col. 2
- (N) p. 6 col. 1
- (P) p. 7, 12; See Reference (B) above
- (Q) HAL_0015054-55



SPE 66553

New Low Viscosity Ester Is Suitable for Drilling Fluids in Deepwater Applications

Kim Burrows, Joannah Evans, John Hall, SPE, and Jeff Kirsner, Baroid Drilling Fluids

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Abstract

High biodegradability and relatively low toxicity have long made esters universally recognized as the best base fluids for synthetic-based muds in regards to environmental performance. A major limiting factor in the use of ester-based fluids, particularly in deep water, is the inherently high kinematic viscosity, a condition that is magnified in the cold temperatures encountered in deepwater risers. These higher viscosities are believed to be especially critical in deepwater wells where lack of overburden causes a severely narrowed window between pore pressures and fracture gradients. Other implications of these higher viscosities include limitations on oil/water ratios, mud weights, and drill solids tolerance.

A new low viscosity (LV) ester has been developed which overcomes these limitations while maintaining the significant environmental advantages of the original esters. The new LV ester has a kinematic viscosity nearly equal to that of currently used internal olefins. It allows formulations of drilling fluids that can be used effectively in virtually all drilling applications in the Gulf of Mexico (GOM), including deep water.

The GOM test protocol was developed to prove the viability of the LV ester as a base fluid. This protocol was designed to consider all conditions drilling fluids are expected to encounter during the course of a well. It evaluates the temperature stability, low temperature rheological properties, and the contamination tolerance of drilling fluids formulated with an LV ester base fluid. Three LV ester fluids were subjected to this protocol: an 11.0 ppg mud; a 14.0 ppg mud; and a 16.0 ppg mud. Results from this extensive laboratory testing indicate new LV ester-based fluids have overcome previous limitations, exhibiting exceptional cold temperature rheological properties, the ability to use a wide range of mud weights and oil/water ratios, and a high tolerance to

contamination. In July 2000, an LV ester-based drilling fluid was used to drill a 3651 ft. interval of a GOM well in 3,669 ft. of water. The LV ester fluid performed well in comparison to the same interval drilled on an offset well with an internal olefin fluid. The initial results from that field trial are included in this paper.

Development of Esters

In 1985, development began on a fully biodegradable base fluid at the request of operators facing restrictions on the use of and discharges from conventional oil base fluids. Esters were found to be the most suitable naturally derived base fluids in terms of potential for use in drilling fluids, being exceptional lubricants, and showing low toxicity and a high degree of both aerobic and anaerobic biodegradability. Ester fluid provides similar shale stabilization and superior lubricity to mineral oil-based mud, and yet also satisfies environmental parameters.

The first trial of the conventional ester-based fluid in February 1990, took place in Norwegian waters and was a technical and economic success. Since then, nearly 400 wells have been drilled worldwide using this C₁₂-C₁₄ ester-based system (Table 1).

The release of ester-based fluids into the global drilling fluids market initiated the era of synthetic-based invert drilling fluids. Following the success of esters, other drilling fluids classed as synthetics were formulated, but these synthetics have not matched the environmental performance of ester-based drilling fluids. One of the most important criteria that they have failed to meet is that of biodegradability; additionally, some have been rejected as a result of poor ecotoxicological or technical performance.

Drivers for Low Viscosity Ester

A low viscosity base fluid was required to give operators the choice of using a system that fulfils more technically demanding requirements than existing ester-based systems, with a particular value in the deeper, colder environments increasingly explored today. The conventional ester is a C₁₂-C₁₄ ester manufactured from palm oil. Research demonstrates that C₈ esters have lower viscosities than their conventional equivalents over a wide temperature range. This led to the development of a lower viscosity C₈ ester base fluid.

Esters have fallen into disuse due to the perception that the elevated viscosities they exhibit at cold temperatures

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contribute significantly to excessive equivalent circulating densities (ECDs), causing an increased risk of lost circulation. This is particularly observed in deep water where long riser lengths are required. The development of an LV ester-based fluid was required to give operators a choice that combines good technical performance with environmental benefits.

Low Viscosity Ester Advantages

Shorter chain length, low viscosity C_8 esters have been developed in response to the increasing importance of viscosity issues as operators move into deeper waters. The viscosity of this fluid is similar to or less than that of other synthetics employed in the Gulf of Mexico.

This offers the following technical advantages:

- Can be used to formulate muds that are stable to 300°F
- Can be used to formulate muds to 16.0+ ppg mud weight
- Can reduce ester/water ratios to 70/30, thus reducing volumes of base fluid discharged
- High tolerance to drilled solids
- Flat gels make it easier to break circulation, minimizing initial circulating pressures and subsequent risk of fracture
- High tolerance to seawater contamination
- Rheological properties can be adjusted by use of additives to suit specific conditions

Substantial testing of this fluid was carried out using a testing protocol designed to simulate conditions to which a fluid may be exposed, including evaluation of temperature stability, low temperature rheological properties, and tolerance to contamination.

LV C_8 Ester Performance

Typically in the GOM, mud is mixed in a mud plant, transported to the rig, and then circulated. While drilling, the mud is exposed to higher temperatures as drilling depth increases. The mud is static in the hole during logging and trips. The fluid must be able to tolerate drill solids and water influxes that may be experienced during drilling operations. In addition, for safety reasons, the drilling fluids must be stable to at least 2.0 lb/gal above the drilling density. The test protocol was developed to simulate and test the effects of those conditions on the LV ester-based fluid.

Three LV ester fluids were subjected to the protocol: an 11.0 ppg mud; a 14.0 ppg mud; and a 16.0 ppg mud. These weights are typical of those used in the GOM. Tests were also run on a 17.0 ppg C_8 LV ester fluid to ensure that the fluid would perform at higher than normal densities.

Temperature Stability. The three muds showed temperature stability from 40°F (4°C) to over 300°F (148°C). This temperature range encompasses the vast majority of operations in the GOM. Fann 75, high pressure and temperature rheological data, indicated yield points of 6, 8, and 8 lb/100ft² at 300°F for the 11.0 ppg, 14.0 ppg, and 16.0 ppg fluid, respectively (Figure 1). These fluids also provide adequate

low end values (6 and 3 rpm) to support suspension of cuttings while maintaining yield points of 50 lb/100ft² or less at 40°F (4°C).

Ester-based fluids should not be used to drill wells that reach temperatures greater than 320°F (165°C). However, fewer than 10% of the wells in Gulf of Mexico are predicted to have temperatures exceeding 320°F (165°C). The majority of these wells are located on the shelf where shipping of cuttings to shore can be readily carried out, or is already necessary due to coastal discharge restrictions.

Mud Density. The use of mud weights exceeding 15.0 ppg for current deepwater applications is rare; however it is possible that higher mud weights will be required. Low viscosity C_8 ester fluids have been successfully formulated to 17.0 ppg (Figure 2).

Ester/Water Ratios. For the GOM protocol, 16.0 ppg and 17.0 ppg LV C_8 ester fluids were formulated and tested with an 80/20 ester/water ratio (EWR). A conventional C_{12} - C_{14} ester-based system would require a 90/10 EWR at these densities due to base fluid viscosity. Flexibility in EWR choices enables the fluid to tolerate water contamination with fewer detrimental effects.

There is also an economic advantage. Based on the amount of oil required per barrel of mud, utilizing a 70/30 EWR versus an 80/20 EWR in an 11.0 ppg fluid reduces the base oil requirement by 12.4% (Figure 3). The cost per barrel is reduced proportionally, and less ester is discharged on cuttings, giving an environmental benefit.

Tolerance to Drill Solids Contamination. The API recommends simulated solids stressing of drilling fluids at a concentration of 35 lb/bbl for mud weights below 15.0 ppg and 20 lb/bbl for muds above 15.0 ppg (API RP13 I, Section 24.6). The GOM protocol solids stressed the muds at concentrations of 20 lb/bbl and 40 lb/bbl. In all three mud weights tested, there were no significant effects on fluid properties. The 14.0 ppg fluid was tested with up to 80 lb/bbl of solids contamination with no detrimental effect on rheological properties. The effects of solids on yield points at 120°F are represented (Figures 4-6).

Cold Temperature Rheological Properties. One of the limitations of the conventional C_{12} - C_{14} ester systems was a high viscosity at temperatures below 40°F. Using the same formulations, the 600 and 300 rpm Fann 75 dial readings are significantly lower for the LV C_8 ester, in comparison to the C_{12} - C_{14} conventional ester (Figure 7).

Using the same testing protocol, the LV C_8 ester fluids demonstrate rheological properties similar to the internal olefin fluids currently being used in deepwater GOM (Table 2).

Breaking circulation. During certain operations, the mud will be static in the wellbore for extended periods. Previous C_{12} - C_{14} ester-based systems became thick, increasing the

pressure required to break circulation. Low viscosity ester fluids do not demonstrate a time-dependent thixotropic behavior, reducing the pressure required to break circulation. The LV C_8 esters exhibit flat gels requiring reduced pressure to re-establish circulation. This helps prevent lost circulation due to fracturing (Figures 8-9).

Seawater Contamination. Testing indicated little change to the yield point values with the addition of 10% seawater to the 11.0 ppg and 14.0 ppg LV ester fluids. At 16.0 ppg, the seawater contamination caused an increase in yield point, as expected, but not unlike what would be found with other synthetic fluids (Figure 10).

First Field Test of LV Ester-Based Fluid

A field test of a low viscosity ester-based fluid took place in July 2000 at a deepwater location in the Gulf of Mexico. The well was situated in 3,669 ft. of water. The LV ester-based fluid was used to drill a 17-in. interval from 5,137 – 8,788 ft MD. The performance of the LV ester-based fluid was compared with the performance of a C_{16}/C_{18} internal olefin fluid used on an offset well drilled by the same operator in the same block. The results of this comparison are provided graphically (Figures 11-14).

Downhole pressures were measured using a Pressure While Drilling (PWD) tool. This is the most effective way in which pressure-related data can be gathered in the well, and in real-time. One of the points of contention with the original ester was the perception that the elevated viscosity in the riser caused abnormally high ECDs, but the real-time PWD data show otherwise. The pressures generated while drilling and under static conditions with the LV ester-based fluid were similar to those generated with the internal olefin fluid (Figures 11-12). The 17-in. intervals on both wells were drilled at similar rates of penetration.

Yield Point. The yield point of the system can be changed. This is important in start-up of circulation which has been identified as the cause of problems such as lost circulation associated with the conventional ester based systems.

New thinning agents have been developed specifically for the LV ester-based system. These products contribute significantly to the performance described here. As measured under ambient conditions at 80°F, after treatment with thinners the yield point on the field test well dropped from 60 lb/100ft² shortly after drilling began to a final yield point of 10 lb/100ft² prior to running casing (Figure 13). ¹⁴

These new thinners are also effective with conventional ester-based fluid systems, thereby increasing the viability of such systems in deepwater environments, where many operators have conventionally considered the viscosities while initiating circulation to be prohibitively high.

Gel Strengths. At 120°F, the LV ester fluid properties reflect the effectiveness of the new thinners. The gels are basically

flat, and the 10-second and 10-minute readings drop significantly after the fluid is treated with thinners (Figure 14). ¹³

LC50 Results. In the 96 hour Mysid shrimp test, the system exhibited excellent LC-50 results for a newly built, lightweight synthetic fluid. The 9.2 ppg non-sheared plant sample had an initial value of 292,700 mg/L. Shearing typically increases the LC50 value, as was the case on the field test. After the interval had been drilled, the LC50 value for the 10.1 ppg LV ester-based fluid was 432,600 mg/L.

Environmental Properties of Esters

As a class, esters have always been recognized for providing the best environmental performance of any synthetic based fluid. Test data demonstrates that the new LV ester exhibits all the advantages typically associated with esters.¹

Aerobic and Anaerobic Biodegradation Testing. The simplest test method is to place the fluid in an aerobic environment and allow the fluids to degrade for a period of time. The extent to which degradation takes place can then be measured.

A better indicator of the extent of degradation expected in the field is the anaerobic biodegradation test. When base fluids become buried in cuttings piles, the available oxygen very quickly falls to zero. As a result degradation is best measured in such anaerobic conditions. Typically, internal olefin degradation under anaerobic conditions as measured by the ECETOC test is 42%, half of that typically measured for both conventional and low viscosity esters (Table 3).^{ii,iii} However, aerobic degradation is measured at similar rates for internal olefin and esters in the BODIS aerobic biodegradation test.^{iv}

Solid Phase Biodegradation Testing. In tests run by the USA EPA, conventional C_{12} - C_{14} ester showed significantly greater degradation than all of the other drilling fluids tested. In contrast internal olefin results could not be easily discerned from other fluids.^v

In concurrent tests completed by the same laboratory, low viscosity C_8 ester showed patterns of degradation similar to those of the conventional ester (Figure 15).

Closed Bottle Testing. The anaerobic closed bottle test indicated one primary result: only ester based drilling fluids biodegrade significantly in a reasonable timespan. It has been suggested that other fluids tested were in a lag phase for periods of up to and including 160 days.⁵ However, if such fluids do not biodegrade in ideal conditions in the laboratory (68°F/20°C) in such a timespan, it is not expected that they will degrade well in colder, anaerobic conditions in the field.

Respirometry. This test indicated that conventional esters degrade significantly better than the other drilling fluids tested.⁵ Esters showed significantly different degradation from diesel, whereas the other drilling fluids did not.

Toxicity Testing

The toxicities of both LV and conventional ester-based fluids are very low, when tested using both U.S. and European test species (Figure 16). For the US *Leptocheirus* 96-hr LC50 test,

which is currently under development, a suite of base fluids was tested simultaneously with the low viscosity C₈ ester and conventional ester so that a comparison of resulting data could be made.

Leptocheirus Testing: 96-Hour. Tests were carried out by an independent laboratory using EPA recommended methods. Note that both ester base fluids are much less toxic than other conventional base fluids (Figure 14).

Leptocheirus Testing: 10-day. A series of representative base fluids and whole muds were run in the 96-hour and 10-day Solid Phase Toxicity test by industry. Again, esters showed superior performance (Tables 4-5).

Seabed Surveys

Seabed surveys taken after the discharge of cuttings from any synthetic-based drilling fluid indicate that there is a smothering effect on the seafloor as the result of deposition of cuttings. As soon as any organic matter present begins to biodegrade, the levels of oxygen are reduced. This has an effect on benthic communities.

However, the biodegradation of esters continues in the absence of oxygen. Cuttings are hydrated and dispersed, aerobic conditions are re-established, and re-colonization by benthic infaunal individuals occurs. The animal communities recover shortly after discharges have ceased.

One year after drilling with an ester-based fluid ceases, subsequent surveys indicate seabed recovery, reflected in species diversity and number, and also in total abundance of individuals.^{vi}

Apart from the rapid recovery of the benthic community, all surveys have shown that the levels of ester in the sediment were below 5,000 ppm in most cases; these were greatly reduced within one year, and two years after drilling, the levels were all but undetectable. Similar patterns of recovery are expected with the LV ester.

Conclusions

The new low viscosity ester-based fluid overcomes all technical criticisms of conventional esters while maintaining the environmental advantages that the systems have always provided.

- The C₈ ester performed well when tested using a protocol designed specifically to simulate GOM conditions.
- When field tested on a GOM well in 3,669 ft. of water, the LV ester-based fluid demonstrated promising performance. Based on PWD measurements, the ester fluid showed lower ECDs than those observed while drilling a comparable interval with internal olefins on an offset well.
- The biodegradation and toxicity performance of esters is "best in class" among all synthetic based fluids. The C₈ ester achieves similar results in these important environmental measures.

Table 1 – Number of Wells Drilled with Ester-Based Fluids Globally

Country	Number of Wells
US	58
UK	56
Norway	64
Nigeria	159
Mexico	5
Malaysia	4
Holland	1
Brunei	4
Australia	32

Table 2 – Rheological Properties of IO Fluids and LV Ester Fluids

	Internal Olefin C ₁₅ -C ₁₈ Fluid	Low Viscosity C ₈ Ester Fluid
11.0 lb/gal, 70/30 EWR, 40°F (4.4°C)		
Plastic Viscosity, cP	65	68
Yield Point, lb/100ft ²	36	27
Fann 35 600 rpm dial reading	166	163
Fann 35 300 rpm dial reading	101	95
14.0 lb/gal, 70/30 EWR, 40°F (4.4°C)		
Plastic Viscosity, cP	86	87
Yield Point, lb/100ft ²	44	53
Fann 35 600 rpm dial reading	216	227
Fann 35 300 rpm dial reading	130	140
16.0 lb/gal, 80/20 EWR, 40°F (4.4°C)		
Plastic Viscosity, cP	85	111
Yield Point, lb/100ft ²	21	36
Fann 35 600 rpm dial reading	191	258
Fann 35 300 rpm dial reading	106	147

Table 3 – Biodegradation of LV Ester and Conventional Ester In Anaerobic and Aerobic Biodegradation Test Protocols

		Anaerobic Biodegradation ECETOC Test (%)	Aerobic Biodegradation 28d BODIS test (%)
INTERNAL OLEFIN BASE FLUID	Result	35	80
LOW VISCOSITY ESTER BASE FLUID	Result	89	81
CONVENTIONAL ESTER BASE FLUID	Result	82	96

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Table 4 – Industry Comparisons between 4-day and 10-day Leptocheirus Tests: Base Fluids				
Base Fluids	Mean 96 hr LC50 Concentration mg/kg	Mean 10 day LC50 Concentration mg/kg	Difference	% Change in Toxicity
Diesel	781	639.4	141.6	18
BB 250	2631	483	2148	82
IO	10288	2829	7459	73
Conventional Ester	21380	13499	7881	37

Table 5 – Industry Comparisons between 4-day and 10-day Leptocheirus Tests: Whole Muds				
Whole Muds	Mean 96 hr LC50 Concentration ml/kg	Mean 10 day LC50 Concentration ml/kg	Difference	% Change in Toxicity
Diesel	1.055	0.86	0.195	19
BB 250	2.9	1.25	1.65	57
IO	28.3	3.5	24.8	88
Conventional Ester	59.5	11.6	47.9	81

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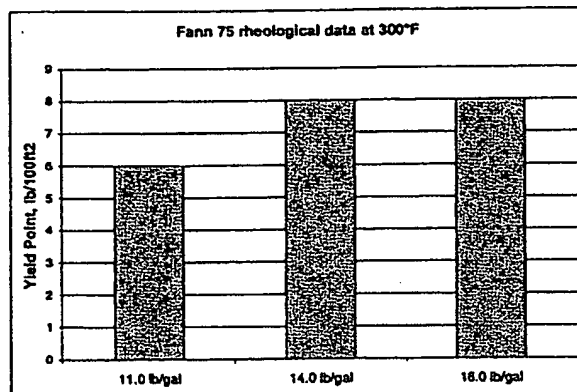


Figure 1 Fann 75 rheological data for low viscosity ester fluid at 300°F.

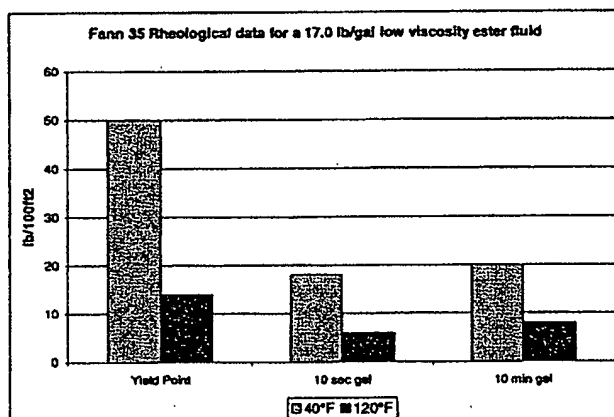


Figure 2 Fann 35 rheological data for 17.0 ppg low viscosity ester fluid.

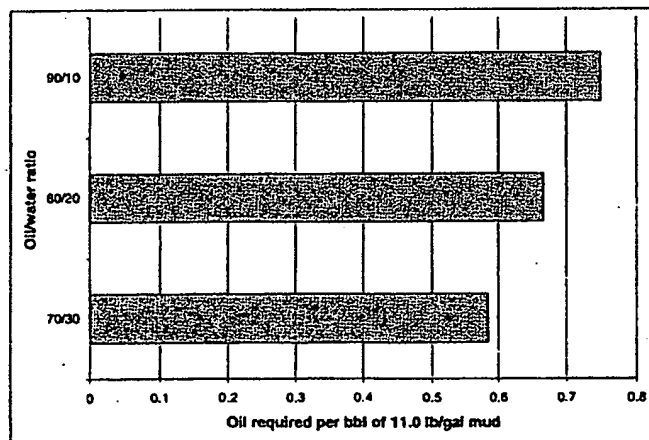


Figure 3 Ester required per bbl of 11.0 ppg mud, varied ester/water ratios.

Figure 4 Effect of drill solids on 11.0 ppg low viscosity ester-based fluid.
Due to their surfactant nature, the thinners in the formulations do not begin to perform until solids are incorporated.

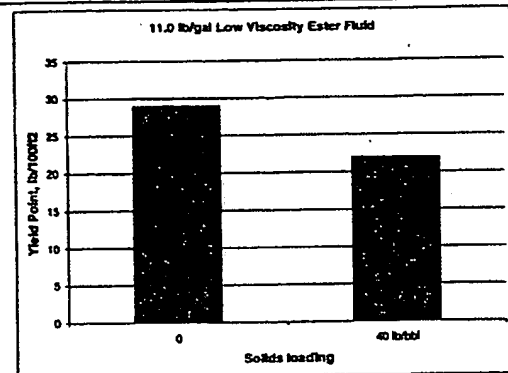


Figure 5 Effect of drill solids on 14.0 ppg low viscosity ester-based fluid.

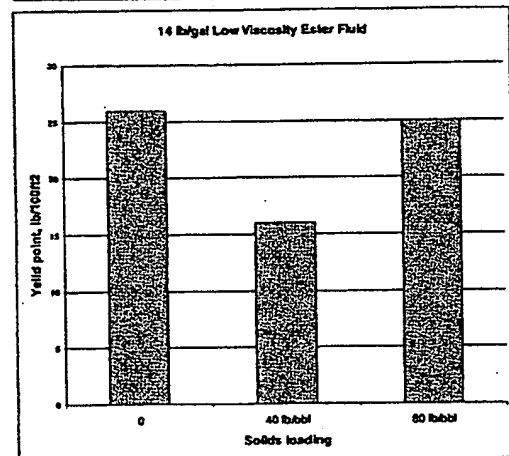
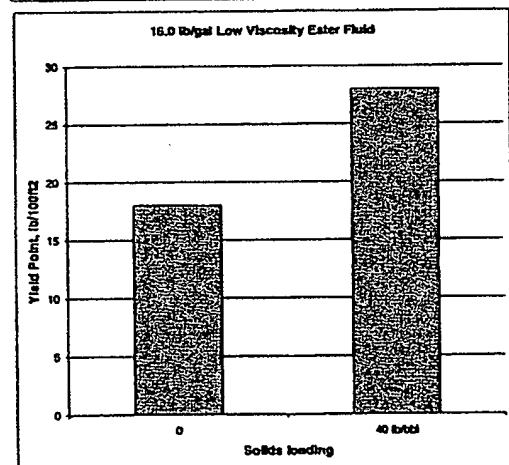


Figure 6 Effect of drill solids on 16.0 ppg low viscosity ester-based fluid.



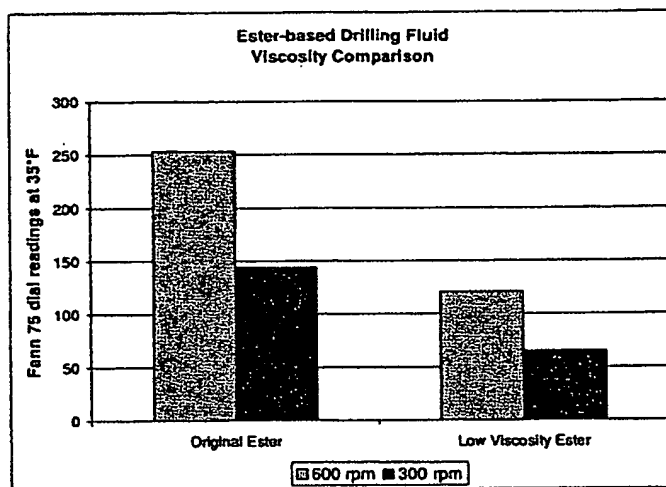


Figure 7 Ester based drilling fluids viscosity comparison.

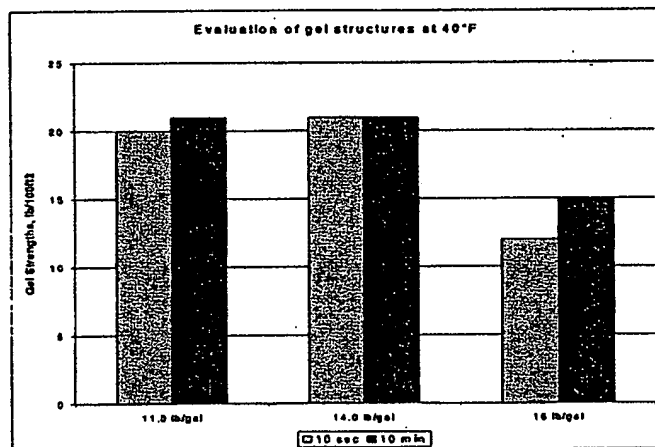


Figure 8 Evaluation of gel structure at 40°F.

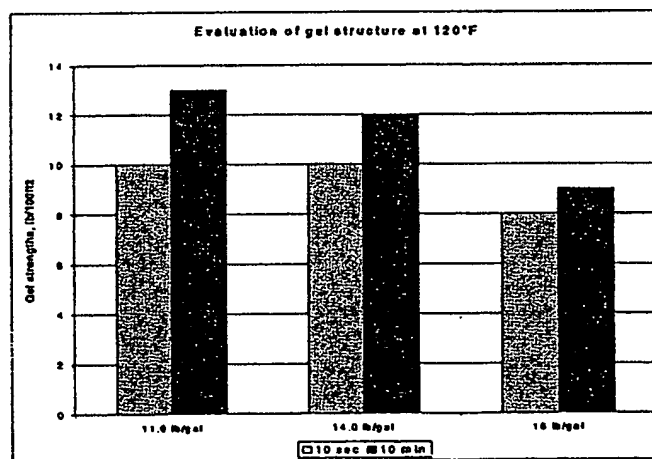


Figure 9 Evaluation of gel structure at 120°F.

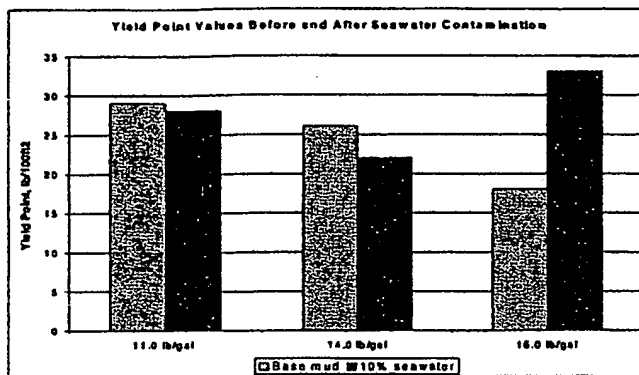


Figure 10 Yield point values before and after contamination.

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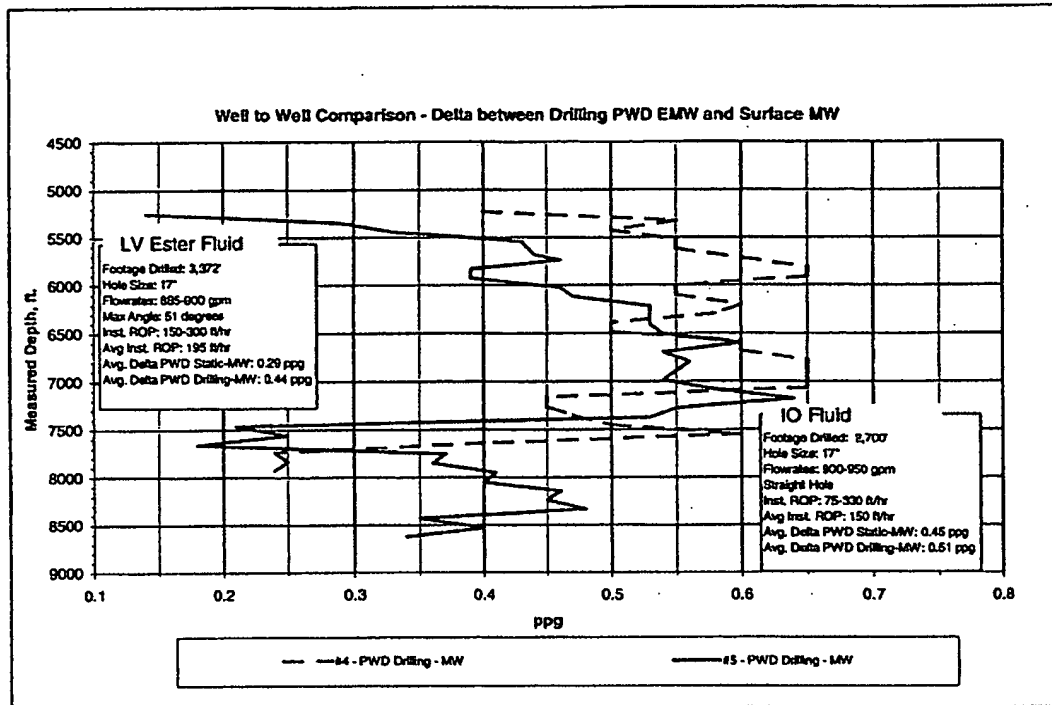


Figure 11 Well-to-well comparison: Delta between drilling PWD equivalent mud weight and surface mud weight.

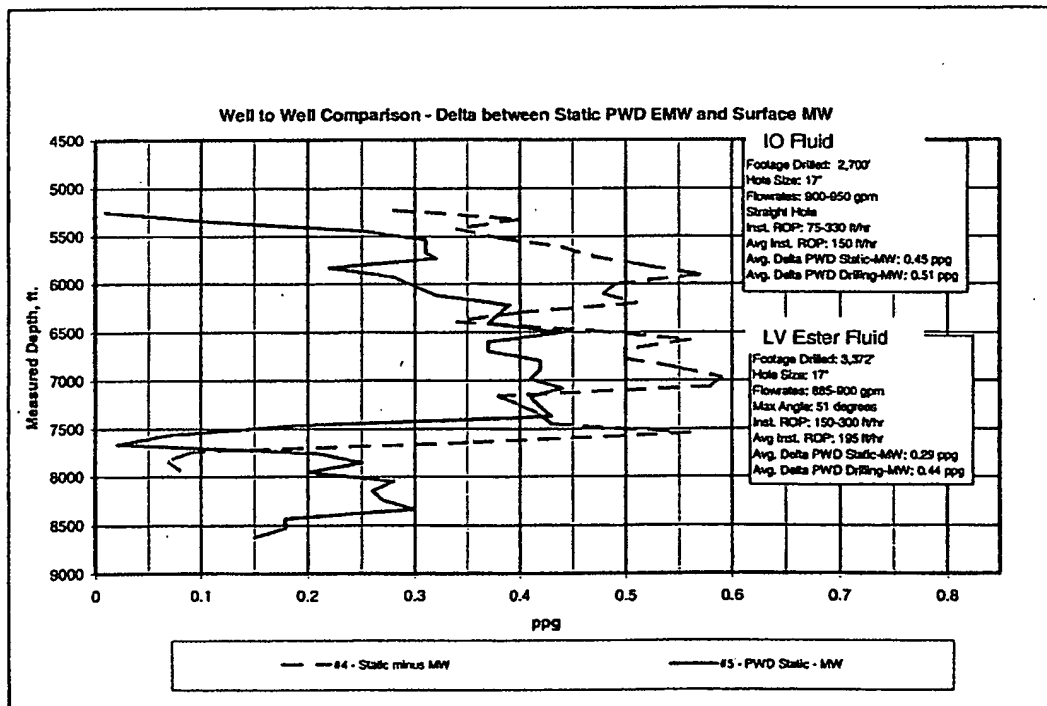


Figure 12 Well-to-well comparison: Delta between static PWD equivalent mud weight and surface mud weight.

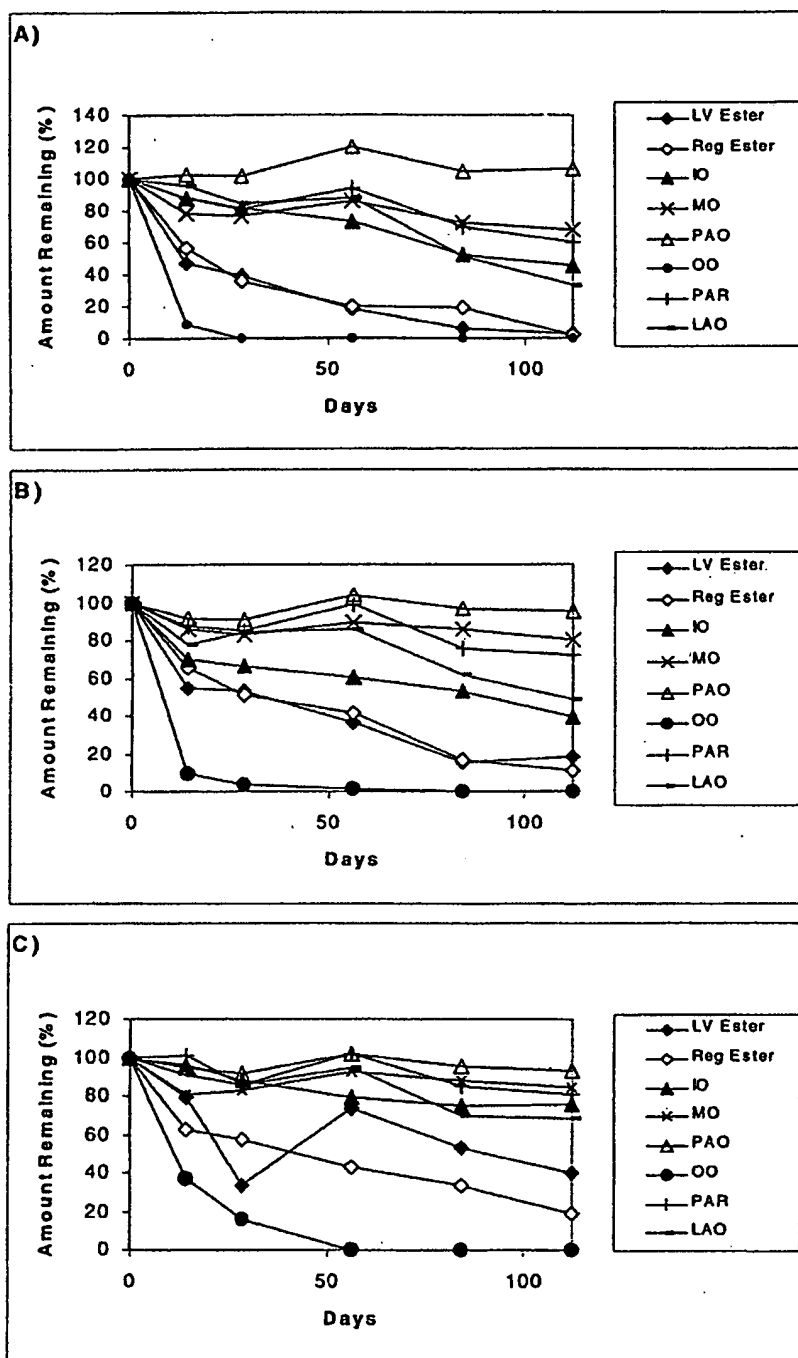


Figure 15 Degradation of esters at 3 different concentrations: a) 1000 ppm; b) 2000 ppm; and c) 5000 ppm.

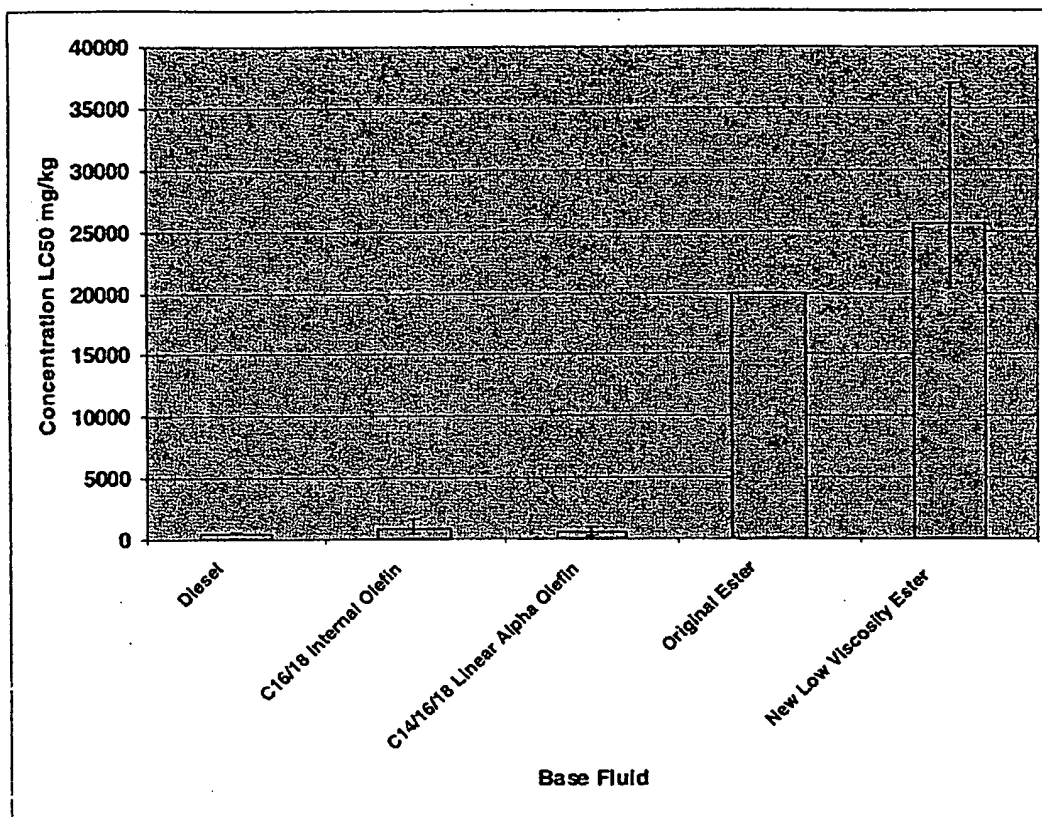
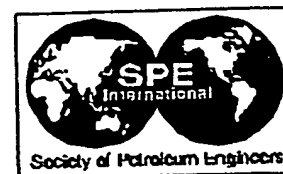


Figure 16 Toxicity performance of esters measured by the 96-hour *Leptocheirus* Solid Phase Toxicity Test in relation to other base fluids commonly used in the US. For the original ester; <50% mortality was observed at a concentration of 20,000 mg/kg, hence no error bar is given as toxicity measured as LC50 is >20,000 mg/kg.

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SPE 65000

High-Density Invert-Emulsion System with Very Low Solids Content to Drill ERD and HPHT Wells

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Abstract

The paper describes the laboratory development of a new Low Solids Oil Based Mud System (OBMS) with a very high specific gravity (2.04 SG; 17 ppg) for high-temperature and high-pressure applications. The system can also be applicable as solid free oil based mud with very low viscosity at densities up to 1.52 SG, especially suggested for Extended Reach Drilling Wells. The main goals of the new system are:

- 1) Optimization of fluid rheology by reduction of the solids contents in the mud.
- 2) Temperature and system stability at 170 °C.

The objectives have been pursued in the following ways:

- by using a very heavy brine as the internal phase;
- by decreasing the oil / brine ratio;
- by using a weighting agent with higher density than barite.

In this way, the amount of weighting solids which needs to be added can be drastically reduced to even below 22% v/v for a 2.04 SG mud, compared to 35% v/v as in traditional oil based muds. Also the PV values have been reduced from typically round 60 cP to even below 25 cP.

The addition of new components to the system has lead to the need of a new emulsifier package, which has been optimized with the development of a primary emulsifier and a wetting agent based on innovative chemistries.

Introduction

Saga Petroleum discovered in 1997 a new high temperature high pressure (HTHP) field offshore Norway, the Kristin field. A total of three exploration wells have been drilled on the Kristin structure. The temperature in the reservoir is 175°C and the pressure 930 bar, requiring the use of drilling fluids with high temperature stability and high density (2.04 kg/l). The drilling of these wells has identified the need of developing a drilling fluid system with better rheological properties and improved temperature stability.

Conventional oil based mud has been used in exploration drilling. In vertical wells the mud has behaved satisfactorily but, when drilling inclined hole, a lot of mud related problems occurred such as barite settling, high equivalent circulating density (ECD) and high surge and swab pressures. To build mud with such high densities, the concentration of weight material needs to be very high. In the wells drilled in the Kristin field the amount of barite was approximately 35% v/v. Together with the drill solids and the organophilic clay, the total amount of solids in the mud was reaching almost 40% v/v. This very high solids content makes it very difficult to achieve a good rheological profile of the mud.

To develop the Kristin field for production several extended reach drilling (ERD) wells need to be drilled. Drilling of these wells cannot be done with this type of mud because of the high ECD, caused by the high rheology of the mud, which might fracture the formation and cause lost circulation problems. The development of a new oil based mud system, which gives far lower ECDs, is therefore essential to be able to drill the necessary wells.

Invert emulsion fluids consist of a salt water solution dispersed into a continuous hydrophobic phase. This emulsion is stabilized by emulsifiers. The salt water phase has traditionally been a CaCl₂-brine, often with lime added for alkalinity. The oil / water ratio is traditionally in the range of 65/45 – 85/15. The concentration of solids in the mud will often dictate the oil / water ratio. In solids laden muds the oil ratio must be high, to keep the solids oil wet and dispersed.

The mud used in the exploration wells of the Kristin field had

an oil / water ratio of 80/20. The water phase used has been CaCl_2 -brine with an S.G. of 1.14. The base oil S.G. was 0.82 and the emulsion S.G. was therefore 0.88. To weight up this emulsion to the desired mud S.G. of 2.04, a total of 35% v/v of barite is needed. The project idea for this new mud system for Kristin has been to reduce the oil / water ratio and to replace the CaCl_2 -brine with a heavier brine. The weight of the emulsion increases and the amount of weighting material needed to achieve the desired mud S.G. is reduced. This heavy emulsion will then be a much better base for building heavy muds with improved rheological properties.

This paper summarizes the findings of the work and suggests a few guidelines for the formulation of a new invert emulsion mud system.

Laboratory Results:

Summary of the work

Three heavy brines have been selected for this study for use as the internal phase in the new mud system:

- CaBr_2 -brine of 1.72 S.G.;
- HCOOK (potassium formate) brine of 1.56 S.G.;
- HCOOCs (cesium formate) of 2.23 S.G.

Muds using formate brines showed to have much better rheological properties than the muds using CaBr_2 -brine; for this reason the results with CaBr_2 -brine are not reported. The CaBr_2 system also seemed to be quite aggressive.

The compatibility between different brines and emulsifiers with different chemistries has been checked, preliminarily by very simple testing (emulsion bottle test), and then confirmed in fully formulated muds.

Compared to the muds previously used in the Kristin field, the oil/brine ratio has been decreased from 80/20 to 60/40 or 50/50. The high brine volume fraction, together with the high salinity of the brines and the surface properties of the selected weighting agent have given quite low electrical stability (ES) values. Nevertheless, stable ES values and low filtrate values have indicated that very good and tight emulsions have been formed. With the optimization of the brine and the oil / brine ratio, the solids content^o of the mud (S.G. 2.04) has been reduced in some instances to even 18% v/v (50/50 Oil/Cesium formate brine ratio).

In addition, different types of weight materials have been tested: manganese tetraoxide, barite and ilmenite. The tests performed with manganese tetraoxide as weighting agent did not show interesting results because the increased surface area of the solids caused a remarkable increase in mud viscosity. The use of ilmenite as weighting material gave better properties of the mud compared to barite. The improvements from using ilmenite are due to the higher density, because a lower volume of solids needs to be added to the system. In addition, ilmenite has a much narrower particle size distribution, with both less small and less large particles, Figure 1. Small particles have higher surface area per volume

and therefore bind up more fluid, which has a negative effect on the rheology. Ilmenite has also no particles above 40 micron while barite specifications call for 3% maximum of the particles to be larger than 74 micron in diameter. Large particles will sag more easily than small particles, thus ilmenite can have less tendency to sag.

Most of the time has been spent to synthesize and characterize new emulsifiers, because it became clear since the beginning that the emulsifier package needed to be tailored to very demanding conditions (different brines, high densities, surface properties of weighting agents, high temperature). Polyamide based emulsifiers showed the best stability at high temperatures. Increasing the polarity of the emulsifiers gave more stable emulsions. Furthermore, the best combination was to use a primary emulsifier with relatively low hydrophilic/lipophilic balance (HLB) values in combination with a secondary emulsifier (or wetting agent) with higher HLB values. Among all the wetting agents synthesized and tested, the most promising was based on a modified imidazoline.

The optimization of the system has also included the evaluation of two different low toxicity mineral oils (synthetic paraffin A and synthetic paraffin B), the screening of different rheology modifiers/fluid loss reducers and the study on the effects of lime in these invert emulsion formulations.

It has been shown that the HPHT filtrates values were already low and could further be reduced with appropriate fluid loss reducers.

These lab muds have been tested for robustness against contamination such as cement, seawater, drill solids etc. and the samples have also been heat aged at 171°C, both dynamically and statically. Ilmenite settling tests have been conducted.

Muds with a higher density (S.G. = 2.2) or with different oil/brine ratio (80/20) were also formulated and characterized. These new systems have proven to be very robust and flexible to all the above mentioned factors giving good confidence for their successful field use.

Also solids free heavy emulsions were studied, focusing on the rheological properties and emulsion stability.

Very good technical results have been obtained with a system based on the following components:

Continuous phase:	Synthetic paraffin B
Internal phase:	Cesium Formate S.G. 2.23 or Potassium Formate S.G. 1.56
Oil/brine ratio:	60/40
Primary emulsifier:	Emulsifier 2137/3
Wetting agent:	WA 11
Fluid loss reducer:	BF 2745
Source of alkalinity:	lime
Weighting material:	ilmenite

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Tests results with Potassium and Cesium Formate

The Tables 1 and 2 report the rheological behavior of muds with potassium formate, Tables 3 and 4 with cesium formate or with a mixed brine 50/50 potassium formate/cesium formate. The influence of several components/contaminants is also reported. The test results show the flexibility of the system by changing the S.G. or the Oil/Brine ratio. The mud with O/B 80/20 requires a higher amount of ilmenite and this is reflected in a higher requirement of suspending agent to avoid settling. The system show a good flexibility by changing density or by using a mixed brine.

The Components of the System

Mineral Oil

At the beginning of the project it was decided to run all the tests with the same mineral oil: synthetic paraffin A. Synthetic paraffin A is based on synthetic pure paraffins and is one of the mineral oils approved for use in the North Sea (OCNF Group Z Base Fluids) because of its low aromatic content. As the project proceeded, another low toxicity mineral oil has been tested. This oil, called synthetic paraffin B, is also based on synthetic pure paraffins and exhibits lower viscosity than synthetic paraffin A. This parameter is negligible when considering invert emulsion with high oil/brine ratio but, as in our case, where the nature of the emulsion is very crowded, the difference of the base fluid viscosity is mirrored in a better rheological behavior of the mud. The PV value can be reduced by 10-15 cP with synthetic paraffin B as reported in Table 5. Therefore synthetic paraffin B has been considered the preferred mineral oil. Table 6 reports the typical properties of the two oils.

Brine

At the beginning of the work a series of different brines were considered before choosing the base-mud formulation for the evaluation of the emulsifier package. The screening has been concentrated on brines characterized by high density, to reduce the volume fraction of the weighting agent in the mud. In Table 7 the typical properties of the brines taken into consideration are reported.

TKPP (tetrapotassium pyrophosphate), after a first test round, has been cancelled because it reacts with lime: calcium pyrophosphate precipitates and depletes the alkali source in the oil phase. CaCl_2 brine is the most common brine used in invert emulsion systems. This brine was not investigated deeply because of its relatively low S.G. The main focus has been on three brines, the CaBr_2 brine of 1.72 S.G., the potassium formate brine (HCOOK) of 1.56 S.G. and the cesium formate brine (HCOOCs) of 2.23 S.G.

By using CaBr_2 -brine (1.72 S.G.) and reducing the oil / brine ratio to 60/40, the weight of the emulsion is increased to 1.18 S.G. and the amount of barite needed to build 2.04 S.G. mud is reduced to 28% v/v. Ilmenite has a density of 4.6 S.G. as compared to barite 4.2 S.G.; by using ilmenite the amount of

weighting material is further reduced to 25% v/v. The use of cesium formate brine (HCOOCs), which has a S.G. of 2.23 will further increase the weight of the emulsion to 1.38 S.G. for a 60/40 oil / brine system, and the amount of weighting material can be reduced to 21% v/v. In this manner it is possible to build heavy mud with drastically improved rheology. If cesium formate brine is too expensive, potassium formate brine (1.56 S.G.) can be considered, in this case the solids volume will be 27% v/v.

Muds using formate brines showed much better rheological properties than the muds using CaBr_2 brine. The CaBr_2 system also seemed to be quite aggressive. The reason for the better rheological behavior of the formate brines is not fully understood. However, it was noticed that formate brines gave relatively low but stable electrical stability values in comparison with bromides and chlorides. This is probably due to the higher salt concentration in the brine.

Formate brines are becoming more widespread in the last years to make up water based drill-in fluids with low solids content and good clay inhibition. This is also due to their good handling and environmental properties. They are in fact biodegradable, non toxic, not corrosive, very user friendly, temperature stable up to 375°F, compatible with the elastomers (Table 8). They have, however, never been reported field-tested in invert emulsion fluids.

Although their price has decreased in the last years, it is still quite high in comparison with chloride or bromide brines. This is particularly true for cesium formate, although it offers more technical advantages because of its higher density. To reduce the cost a mixed brine 50/50 HCOOK/HCOOCs has been tested. The compatibility between the two brines at all the ratios has been verified with good results. Keeping in mind that these muds can be reconditioned and reused in many wells, the cost per well can be further lowered.

Separate studies conducted by Cabot⁽⁴⁾ and Shell have shown that the solubility of barite in cesium formate was in the range of 600-700 mg/l. The solubility testing clearly shows that in field operations contamination of used cesium salt solutions with barium salts is likely. During this project this problem has been overcome by using ilmenite instead of barite.

Lubricity test results conducted by Cabot with a HLT Lubricity Testing Instrument and a Baroid Lubricity Meter⁽⁴⁾ indicate that both potassium and cesium formate base fluids are extremely lubricious, significantly reducing the coefficient of friction values of metal-to-metal, metal-to-sandstone, and metal-to-shale contact surfaces. The coefficient of friction for formate based fluids was lower than that of mineral oil based invert emulsion fluids based on CaCl_2 brine. Even if formate is the internal phase of the emulsion, it could be argued that invert emulsions formulated with formate brines are very promising to drill extended reach and deviated holes where a low coefficient of friction is needed.

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Weighting Material

For more than 60 years barite has been the main weighting material for muds. There are several reasons for its popularity:

- The high specific gravity (S.G.=4.2) permits weighting the mud with as little increase in solids as practical.
- Its chemical inertness and virtual insolubility in water or oil minimizes effects on mud properties and the environment.
- Barite's intermediate hardness (2.5-3.5 Mohs Scale) is soft enough to prevent serious abrasion of metal but hard enough to prevent excessive attrition and creation of fines.
- It is available in large quantities at low cost to meet the industry requirements of millions of tons per year.

Of all the additives used in the formulation of oil well drilling fluids, the weighting material is used in the largest quantity. Over the past few years iron oxides have come into use as weighting material, such as hematite, ilmenite, itabirite and Fer-O-Bar; among them ilmenite is the most promising. Ilmenite is an iron-titanium oxide and has higher specific gravity than barite and higher hardness (Table 9). During past uses of ilmenite as a weighting agent in WBM, the abrasion on drilling equipment has been of greatest concern because of the harder nature of ilmenite. Many studies have addressed this problem (Geocare, Internal Report, 1997 ⁽⁶⁾ Haaland et al., 1976 ⁽⁷⁾; Blomberg et al., 1984 ⁽³⁾). In general, field observations have been confirmed by laboratory experiments. However, the abrasiveness is highly dependent on the particle size distribution (average and maximum particle size) and experiments clearly show that the abrasiveness of ilmenite can be reduced to that of standard barite by removing the largest particles. It was found (Blomberg et al., 1984 ⁽³⁾) that with less than 3% particles > 45 micron abrasion could reach acceptable values. Furthermore, ilmenite in oil based drilling fluids showed much lower abrasion.

The ilmenite now available on the market meets this limit. The ilmenite used during this project is produced in South Rogaland, Norway from a hard rock ilmenite ore. The concentrate contains ca. 94% ilmenite with the silicates hypersthene and plagioclase as the main accessory minerals. Ilmenite has lower concentrations of heavy metals such as lead, barium and copper than barite, but is higher in other metals such as chromium and nickel. Studies on flatfish have shown that no metals from ilmenite are bioavailable, although lead, barium and in cases cadmium may be available from barite. Ilmenite is included in the SFT List A of the approved products to be used in the North Sea Norwegian Sector.

The breakdown of barite or other weighting material into smaller particles, can reduce the quality of drilling fluid. The increase of the number of very fine particles results in an increase in the drilling fluids viscosity and reduced penetration rate. If viscosities become too high, the very fine particles must be removed by use of a centrifuge. The particle size distribution of ilmenite (Figure 1), between 6 and 45 micron,

would not result in drilling fluid loss by centrifuge treatment. Because ilmenite is harder than barite, it does not break down to smaller particles as easily as barite. Virtually no attrition will occur for ilmenite during mechanical working, meanwhile barite normally becomes finer grained. During attrition the total number of particles in a drilling fluid may increase to a point where the particles come in contact with each other, and therefore the viscosity of the fluid increases. Attrition by mechanical grinding may result in more rapid increases of yield points and gel strengths for barite containing fluids than for ilmenite containing fluids.

The importance of penetration rates on overall well costs in drilling is widely recognized. If rig time is reduced by higher rates of penetration, overall cost is generally reduced. It is well known from literature (Rupert et al., 1981⁽¹⁶⁾; Blattel et al., 1982⁽²⁾) that the use of ilmenite in drilling fluids (both water based and oil based) can drastically enhance the penetration rate. Based on laboratory and field studies, in fact, the properties of drilling fluids that primarily affect the rate of penetration are viscosity, filtrate loss and solids content. With higher specific gravity weighting material than barite, a lower solids content is needed to obtain the needed drilling fluid S.G. With fewer solids in the system, the particles are allowed to disperse further apart, thus lowering the plastic viscosity. A higher specific gravity weighting material, such as ilmenite, would lead to increased penetration rate, based on its effects on rheology.

Barite is considered partially soluble in formate brines such as those used in this project, therefore it can not be used as weighting material in these kind of fluids. Ilmenite is considered relatively insoluble in formate brines.

In aqueous solutions crystal surfaces are electrically charged. This property determines the state of particle dispersion, rheology of suspensions and whether the particle acts as an absorbent or ion exchanger. The term zeta-potential is used to quantify this property and is considered as the drop in charge across the diffuse layer in an electrolyte. For each particle, the zeta-potential is dependent on the pH and the dissolved ions in the aqueous fluid. Ilmenite displays a zeta-potential pattern typical of oxide minerals with a low zeta-potential at high pH conditions, whereas barite has a more stable zeta-potential. At high pH, such as common for drilling fluids, the surface charge of ilmenite will therefore result in dispersion within the drilling fluid. For barite under similar conditions, particles will not be dispersed and will actually come in contact with each other so that van der Waals' bonding between crystals may occur. Van der Waals' attraction between particles would cause agglomeration of particles and would also affect rheological properties of drilling fluids.

Other advantages of ilmenite as weighting material include solubility in acids, reaction with sour gases, less fine particles, very low attrition rate and no appreciable settling. This result in a stable rheology with limited need for dilutions and

chemical conditioning, therefore allowing lower drilling fluid maintenance costs. Table 10 shows the results of the same mud formulated with barite or ilmenite.

Emulsifier Package

The synthesis of the primary emulsifiers was focused on polyamides because this is the chemical class that shows the best stability at high temperatures. Starting from polyamides with known performance in invert emulsion muds at high oil / brine ratio and high temperature, polyamides were synthesized with different molecular weight (MW), hydrophilic-lipophilic balance (HLB), different polarity and fatty acid sources. The starting point polyamides showed high viscosity of the system and / or unstable emulsions when very heavy brines were used. This fact is particularly evident with calcium salts, whereas potassium formate brines gave lower viscosities but with lower electrical stability before and after aging. It was shown that not all the emulsifiers normally used and available on the market are able to tolerate variable oil / brine ratio ranging from 90/10 to 50/50.

All the emulsifiers synthesized have been formulated in a suitable solvent, at the same active content and characterized. The emulsifier concentration has been optimized testing different concentrations (Table 11).

During the project it was realized that also a wetting agent with higher HLB was needed to control the rheology of the system. A separate evaluation has been performed to develop an appropriate wetting agent. A number of surfactants have been synthesized and evaluated with different types of chemistries and hydrophilic/lipophilic properties. The two products that have shown the best behavior were Emulsifier 2137/3 (Primary emulsifier) and WA 11 (Wetting agent).

Lime

Ilmenite reacts with sour gases, such as H_2S , that may be encountered during drilling. Because of that, lime is theoretically not needed in the developed system. Nevertheless some tests have been performed to establish the properties' variation of the base mud by addition of an alkali. Alkaline substances are used to block acidic influxes, such as hydrogen sulfide, carbon dioxide or the products of degradation of organic compounds; in addition, the calcium salts of fatty acids are known to be water in oil emulsifiers. Besides lime, potassium hydroxide was used to verify any possible difference due to the precipitation of calcium formate with lime. The addition of lime has been found to be beneficial to the stability of the emulsion and to the filtrate (Table 13 and 14).

Rheology modifier

Some different rheology modifiers have been screened during the project. Products based on fatty acid polyamides, tall oil dimer acids or synthetic polymers have been tested without interesting results. Rheology modifiers are not required in the system because rheology and suspending properties of the

mud can be adjusted by selecting the right oil / brine ratio and the organoclay concentration. Furthermore, by using heavy brines and a heavy weighting agent the amount of solids to suspend can drastically be reduced. The particular size distribution of ilmenite is such that ilmenite is easier to suspend than barite.

Fluid Loss Reducer

High-pressure high-temperature fluid loss (500 psi, 340°F) has been investigated only once the rheology had been optimized. Filtrate optimization was in fact not one of the main goals of this project.

The emulsion formed by Emulsifier 2137/3 is already strong and tight enough to give relatively low filtrate values (7-8 ml for the base muds) even at this high temperature without any filtrate reducer. Anyway, both commercially available fluid loss reducers and newly developed products have been tested. Fluid loss reducers commonly used in invert emulsion fluids are based on gilsonite (a naturally occurring weathered asphalt), amine-treated/causticized lignite, pliolite or polybasic acids. Among this range, polybasic acids have shown to be not stable at 340°F; the filtrate can therefore be controlled with the other types of chemicals.

New products have been synthesized, based on crosslinked polyacrylate esters in emulsion form, with different degrees of crosslinking. One of these products, called BF 2745 (Table 15), has shown to be extremely effective in controlling the filtrate even at very low dosages (Table 16 and 17). The thickness of the mud cakes were few mm and always proportional to the filtrate volume.

Organophilic clay

An organically modified clay (HT organoclay) has been used for all the tests as viscosifier / suspending agent (Table 18). HT organoclay is a highly purified smectite clay (hectorite), reacted with quaternary ammonium compounds to become oil soluble. This HT organoclay is normally used in HPHT wells because of its good thermal stability. Water is needed to act as activator to ensure full development of the rheological properties in the fully formulated mud.

A HT organoclay particle consists of a clay platelet having a long-chain organic compound (quaternary ammonium salt) bonded to its two faces. In the system containing the fully dispersed and activated organoclay additive, a gel structure is developed by edge-to-edge hydrogen bonding between hydroxyl groups on the organoclay platelet edges. The hydroxyl groups on adjacent organoclay platelets edges are bridged by water molecules, forming a three-dimensional gel structure. If the water bridge is not present, no gel structure is developed. Solvation of the long chain organic molecule tails makes them stand away from the clay platelet faces. To obtain full rheological effectiveness, the hydrogen bonding sites on the HT organoclay platelet edges should not be obstructed. The concentration of HT organoclay required in the system

has always been very low. Because of the high density and low oil / brine ratio, most of the viscosity is contributed by the solids and by the water droplets dispersed in the continuous oil phase. It has been demonstrated that changing the oil / brine ratio from 60/40 to 80/20, the HT organoclay concentration needs to be increased from 1 pound per barrel (1 ppb / 2.9 kg/m³) to 8 ppb (22.9 kg/m³) to obtain the correct rheological parameters and avoid ilmenite settling.

Comparison of fluid rheology with traditional field muds.

Figure 2 shows the rheological profile of muds used during drilling on Kristin compared to muds developed in this project. Well 6406/2-5 was a vertical well where the mud apparently behaved satisfactorily without any mud-related problems. The same mud was used in well 6406/2-5AT2 where the inclination was 35°. Excessive barite sag was observed and the rheology was therefore boosted to compensate. The result was mud with very high viscosity readings at high shear rates as shown in the figure. This mud had very high ECD and high surge and swab pressures, with problems during drilling and cementing of the liner.

The desired rheology profile of muds for drilling ERD wells is flat, with high readings at low shear rates (typically 10-12 at 3 rpm) to hinder sagging of weighting material and low viscosity at high shear rates to give minimum ECD. As demonstrated in the figure, a dramatic improvement of the rheology is obtained for the new mud systems developed in this project. By using advanced software for calculating ECD during drilling, the effect of shifting to this new mud system is shown to be a reduction in ECD increment of 50-60% compared to the mud used in well 6406/2-5AT2. This improvement can make it possible to drill ERD wells at Kristin with ECDs lower than the fracture pressure.

Possible Applications and Future Developments

During drilling, formation damage may occur by plugging of pore spaces with drilling fluid additives. Treatment with HCl acid is commonly used to remove the plugging minerals but, because of barite's virtual insolubility, formation permeability can not be easily restored. Ilmenite on the other hand is reactive with HCl and therefore would allow formation permeability to be restored; in addition size distribution of ilmenite should be ideal for minimizing formation plugging and damage.

For special applications, the weighting material can be totally eliminated from the fluid. Solids free heavy emulsions are very interesting drill-in fluids, since they will cause no formation damage due to the weighting material, such as it is often seen from barite. Furthermore, all formate brines are based on monovalent cations (Sodium, Potassium, Cesium) which eliminate the risk of damage due to scale formation.

Even though this mud system has been designed specifically for HTHP drilling, the fluid system based on heavy emulsions can have other applications. By using cesium formate and an

oil / brine ratio of 50/50, mud weight of 1.52 S.G. can be obtained without addition of weighting material. This can be a very interesting fluid since suspension of weighting material will no longer be required. The viscosity can be lowered, giving a mud which could be very interesting for drilling in areas with very narrow ECD limits, for slim hole drilling and for coiled tubing drilling.

The advantages of solids-free heavy emulsions are significant. The plastic viscosity of muds is greatly affected by the quantity of suspended solids. Solids free emulsions systems will exhibit lower plastic viscosities than conventional mud systems. This will result in lower equivalent circulating densities (ECDs) and lower parasitic pressure losses down-hole, resulting in greater drilling efficiency. These two effects are particularly important in slim hole drilling and coiled tubing where, because of the reduced pipe and annulus diameters, minimizing down-hole pressure losses (and hence ECDs) is essential to ensure good rates of penetration, while preventing the fracturing of the formation. Some test results of solids free emulsions are reported in Table 19. Only Emulsifier 2137/3 is used at a concentration of 18 g in 400 ml emulsion (45 kg/m³). Rheology is very stable before and after hot rolling and is not dependent on the S.G. but only on the oil / brine ratio.

Conclusions

A low solids oil based mud system has been developed by the use of heavy brines in the internal phase and by using a high brine content to give a heavy emulsion as a base for the mud system.

The systems have been tested and proven stable at temperatures as high as 170 °C.

By using cesium formate in the internal phase and ilmenite as weighting agent, 2.04 SG HTHP mud with solid content as low as 21% v/v was developed. This mud has very low rheology with a PV below 25 cP and gives a tremendous reduction in ECD during drilling compared to conventional oil based muds used up to date.

Solid free oil based mud of densities as high as 1.52 SG and with extremely low rheology can also be made using the same chemical package as developed for the HTHP mud. This solid free system can be very interesting for drilling of wells with very narrow ECD limits, for slim hole drilling and for coiled tubing drilling.

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Nomenclature

YP	Yield Point [lb/100ft ²]
PV	Plastic Viscosity [cP]
AV	Apparent Viscosity [cP]
BHR	Before Hot Rolling
AHR	After Hot Rolling

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Table 1 - Tests with Potassium Formate

Formulation (base mud) :

Synthetic Paraffin B
Emulsifier 2137/3
Wetting agent WA 11
HT Organoclay
Brine HCOOK 75% d = 1.56
ILMENITE

9
112
18
4
1
141.7
435

Oil / Brine ratio 60/40
S.G. 2.04
Ilmenite vol. % 27.5

Measurements at 120 F BHR

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	80	48	37	24	7	6	6	6	40	32	16	274
3 ppb lime	90	53	39	26	8	7	7	7	45	37	14	350
1 ppb BF 2745	101	61	47	31	10	8	8	8.5	50.5	40	21	250
20 ppb OCMA clay	118	69	53	34	10	8.5	9	9	59	49	20	250
35 ml seawater	100	58	44	29	8.5	7	7	8	50	42	16	230
35 ml cement slurry**	114	65	48	30	8	7	7	7	57	49	16	250

Measurements at 120 F AHR 16h at 340 F (170°C)

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	98	62	49	33	11	9.5	10	10	49	36	26	210	11.6 (0.6+2.4)*
3 ppb lime	93	56	44	30	10	9	9	9	46.5	37	19	330	7.2 (0.8)*
1 ppb BF 2745	102	68	53	35	12	10	10	11	51	34	34	220	6.8 (0.4+0.6)*
20 ppb OCMA clay	135	90	71	48	15	13	13	13	67.5	45	45	225	18.4 (0.8+5.2)*
35 ml seawater	123	76	60	41	13.5	11	11	11	61.5	47	19	235	17.6 (1.2+4.8)*
35 ml cement slurry**	125	77	58	39	12	10.5	11	11	62.5	48	29	265	10 (0.8+1.2)*

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

** cement slurry has been formulated with 66% cement Class G-HSR and 44% liquids v/v with fresh water, dispersant, fluid loss reducer and aged at 60-80 °C for 1 h.

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Table 2 – Test with Potassium Formate

Formulation :

	g	g
Synthetic Paraffin B	103.5	142.8
Emulsifier 2137/3	18	18
Wetting agent WA 11	4	4
HT Organoclay	1	8
Lime	3	0
Brine HCOOK 75% d = 1.56	133.6	69.1
ILMENITE	506.7	479

Oil / Brine ratio	60/40	80/20
S.G.	2.2	2.04
Ilmenite vol. %	32.2	30.4

Measurements at 120 F BHR

	HT Organoclay	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
S.G. 2.2; 60/40	1 ppb	115	67	50	33	9	8	8	8	57.5	48	19	370
S.G. 2.04; 80/20	4 ppb	61	35	26	17	6	5	5	6	30.5	26	9	255
S.G. 2.04; 80/20	8 ppb	79	48	37	25	9	8	8	10	39.5	31	17	280

Measurements at 120 F AHR 16h at 340 F (170°C)

	HT Organoclay	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
S.G. 2.2; 60/40	1 ppb	127	78	60	40	13	11	11	11	63.5	49	29	310
S.G. 2.04; 80/20	4 ppb	55	30	23	14	5	45	5	6	27.5	25	5	300
S.G. 2.04; 80/20	8 ppb	88	54	41	26	8	7	7	9	44	34	20	240

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Table 3 – Test with Ceslum Formate

Formulation :

Synthetic Paraffin B
Emulsifier 2137/3
Wetting agent WA 11
HT Organoclay
Brine HCOOCs d =2.23
ILMENITE

9
122.2
18
4
1
229
339.7

Oil / Brine ratio 60/40
S.G. 2.04
Ilmenite vol. % 21.6

Measurements at 120 F BHR

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	60	35	27	18	6	5	5	5	30	25	10	270
3 ppb lime	59	34	25	16	5.5	4.5	4.5	5	29.5	25	9	370
1 ppb BF 2745	71	43	32	21	7	6	6	6.5	35.5	28	15	290
20 ppb OCMA clay	80	49	37	25	8	7	7	7	40	31	22	340
35 ml cement slurry**	75	42	30	19	5	4	4	5	37.5	33	9	200

Measurements at 120 F AHR 16h at 340 F (170°C)

Added component	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	86	54	43	29	9	8	8	8	43	32	22	185	13.6 (0.4+3.6)*
3 ppb lime	62	38	29	20	7	6	6	7	31	24	14	350	8 (0.5+0.5)
1 ppb BF2745	74	47	36	25	8.5	7	7	7.5	37	27	20	270	8 (0.2+0.6)*
20 ppb OCMA clay	96	57	41	21	8	6.5	6.5	7.5	48	39	18	180	18.6 (1+2.8)*
35 ml cement slurry**	85	50	38	25	8.5	7	7	8	42.5	35	15	230	17.8 (1.4+4.4)*

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

** cement slurry has been formulated with 66% cement Class G-HSR and 44% liquids v/v with fresh water, dispersant, fluid loss reducer and aged at 60-80 °C for 1 h.

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Table n. 4 – Tests with Cesium Formate

Formulation :

	g	g
Synthetic Paraffin B	113	116.5
Emulsifier 2137/3	18	18
Wetting agent WA 11	4	4
HT Organoday	1	1
Lime	3	3
Brine HCOOCs d = 2.23	212	-
Brine 50/50 K/Cs Formate d = 1.90	-	182
ILMENITE	419	392.5

Oil / Brine ratio	60/40	60/40
S.G.	2.2	2.04
Ilmenite vol. %	26.6	24.8

Measurements at 120 F BHR

S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
2.20	73	42	31	20	6	5	5	6	36.5	31	11	330
2.04	74	44	33	21	6.5	5.5	6	6	37	30	14	360

Measurements at 120 F AHR 16h at 340 F (170°C)

S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
2.20	84	51	39	27	9	8	8	8	42	33	18	320
2.04	80	50	39	27	10	9	9.5	9.5	40	30	20	290

Table n. 5 – Comparison Between Two Different Mineral Oils

Oil/Brine 60/40; S.G.: 2.04; Measurements at 120 F BHR

Base oil	Weighting agent	Wett. agent	600	300	200	100	6	3	G ₀ /G ₁₀	AV	PV	YP	ES
Synt. Paraffin A	Ilmenite	WA02	96	52	37	21	4	3	3/5	48	44	8	275
Synt. Paraffin B	Ilmenite	WA02	74	40	28	16	3.5	3	3/4	37	34	6	270

Measurements at 120 F AHR 16h at 340 F (170°C).

Base oil	Weighting agent	Wett. agent	600	300	200	100	6	3	G ₀ /G ₁₀	AV	PV	YP	ES
Synt. Paraffin A	Ilmenite	WA02	118	62	44	26	6	4	5/6	59	56	6	340
Synt. Paraffin B	Ilmenite	WA02	84	46	33	19	5	4	5/5	42	38	8	264

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Table n. 6 – Typical Properties of Two Different Mineral Oils

Property	Synthetic Paraffin A	Synthetic Paraffin B	METHOD
Density @ 15°C	814 g/l	811 g/l	ASTM D 4052
Saybolt color	+ 30	+ 30	ASTM D 156
Boiling Range:			ASTM D 86
- Initial point	255°C	231°C	
- Dry Point	325°C	265°C	
Flash Point	118°C	101°C	ASTM D 93
Viscosity @40°C	3.5 mm ² /sec	2.28 mm ² /sec	ASTM D 445
Total Aromatic Content	0.003%	0.001%	UV
Aniline Point	91°C	80°C	ASTM D 611
Pour Point	- 27°C	- 51°C	ASTM D 97
Sulfur Content	0.5 ppm	0 ppm	ASTM D 3120
Auto ignition temperature	> 230°C	> 230°C	ASTM E 659
Vapor pressure	0 mbar @ 37.8°C	> 0.01 kPa @ 20°C	
CAS No.	64741-77-1	64742-46-7	
EINECS No.	265-078-2	265-148-2	
Biodegradability	76.5%	95%	OECD 306
Aquatic toxicity:			ISO/PARCOM GL
- Acartia Tonsa	LC50> 42.900 mg/l	LC50: 65.155 mg/l	ISO/PARCOM
- Skeletonema Costatum	EC50>100.000 mg/l	EC50>100.000 mg/l	

Table n. 7 – Typical Properties of Different Brines

Brine	Concentration	S.G.	MW	M (mol/l)	Aw
CaCl ₂	40 %	1.40	111	5.15	0.39
CaBr ₂	52%	1.72	199.9	4.47	ND
TKPP	ND	1.73	330.4	ND	ND
HCOOK	75%	1.56	84.1	14.09	0.31
HCOOCs	82%	2.23	177.9	10.51	0.28
50/50 HCOOK/HCOOCs	78.5%	1.90	n.a.	n.a.	0.29

Table n. 8 – Typical Properties of Formate Brines

Property	HCOOK	HCOOCs H ₂ O
Biodegradation (OECD 301-D)	92%	83%
Theoretical Oxygen Demand	3.42 mgO ₂ /l	4.05 mgO ₂ /l
EC ₅₀ 48 h with <i>Acartia Tonsa</i>	300 mg/l	340 ml/l
LC ₅₀ 72 h with Brown Shrimp (<i>Crangon Crangon</i>)	1300 ml/l	91 ml/l
LC ₅₀ 96 h with Rainbow Trout	3500 ml/l	2100 ml/l
EC ₅₀ 72 h with <i>Skeletonema Costatum</i>	3400 ml/l	1000 ml/l
HOCNS Classification for the North Sea	E	E

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Table n. 9 – Typical Properties of Two Different Weighting Agents

Property	Barite	Ilmenite
Chemical formula	BaSO ₄	FeTiO ₃
Specific Gravity	4.2-4.5 (normally 4.2)	4.5-5.1 (normally 4.6)
Hardness (Mohs Scale)	2.5-3.5	5-6
Particle size	<3% >74 micron <30% <6 micron	<3% >45 micron <10% <1micron
Acid solubility	Insoluble	Soluble
Hardness (Mohs Scale)	2.5-3.5	5-6
Crystal structure	Orthorhombic	Hexagonal

Table n. 10 – Mud Rheology with Two Different Weighting Agents

Oil/CaBr₂ Brine 60/40; S.G. 2.04; Measurements at 120° F BHR

Emulsifier	Wetting agent	Weighting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
2137/3	WA02	Ilmenite	96	52	37	21	4	3	3	5	48	44	8	275
2137/3	WA02	Barite	112	59	41	23	4	4	4	5	56	53	6	1000

Measurements at 120 F AHR 16h at 340 F (170°C).

Emulsifier	Wetting agent	Weighting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT (ml)
2137/3	WA02	Ilmenite	118	62	44	26	6	4	5	6	59	56	6	340	8
2137/3	WA02	Barite	126	69	48	29	7	6	6	6	63	57	12	620	N.D.

Table n. 11 – Mud Rheology with Increasing Concentrations of Primary Emulsifier

Oil/K formate brine 60/40; S.G. 2.04; Measurements at 120 F BHR

2137/3 concentration	Wetting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
14 ppb	WA11	76	43	32	20	5,5	4,5	5	6	38	33	10	260
18 ppb	WA11	80	48	37	24	7	6	6	6	40	32	16	274
22 ppb	WA11	80	48	37	25	8	7	7	8	40	32	16	282

Measurements at 120 F AHR 16h at 340 F (170°C)

2137/3 Concentration	Wetting agent	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
14 ppb	WA11	124	81	64	45	14	12	10	11	62	43	38	155	15,8 (1+3)*
18 ppb	WA11	98	62	49	33	11	9,5	10	10	49	36	26	210	11,6 (0,6+2,4)*
22 ppb	WA11	92	58	46	31	10,5	9	9	9	46	34	24	244	10 (1)

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

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Table n. 12 – Typical Properties of the Primary and Secondary Emulsifier

Property	Emulsifier 2137/3	WA 11
Chemical description	Modified fatty acids polyamide	Modified imidazoline
Appearance	Viscous dark liquid	Orange liquid
Acid Number	30-35 mg KOH/g	50-60 mg KOH/g
Amine Number	9.5 mg KOH/g	22 mg KOH/g
Brookfield Viscosity	1800 cP	15 cP
Pour Point	< -10°C	< -10°C
Flash Point	> 79°C	> 60°C
Water solubility	Insoluble	Soluble
HLB (estimate)	3-7	8-11

Table n. 13 – Influence of Alkali in Potassium Formate Mud

Measurements at 120 F BHR

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	80	48	37	24	7	6	6	6	40	32	16	274
3 g Lime	90	53	39	26	8	7	7	7	45	37	14	350
2.5 g KOH	81	47	35	23	7	6	6	6	40.5	34	13	350

Measurements at 120 F AHR 16h at 340 F (170°C)

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	98	62	49	33	11	9.5	10	10	49	36	26	210	11.6 (0.6+2.4)*
3 g Lime	93	56	44	30	10	9	9	9	46.5	37	19	330	7.2 (0.8)*
2.5 g KOH	88	52	40	26	9	8	8	8	44	36	16	270	9 (0.4+1.6)*

* HPHT filtration at 340 F (170°C), 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

Table n. 14 – Influence of Alkali in Cesium Formate Mud

Measurements at 120 F BHR

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	60	35	27	18	6	5	5	5	30	25	10	270
3 ppb Lime	59	34	25	16	5.5	4.5	4.5	5	29.5	25	9	370

Measurements at 120 F AHR 16h at 340 F (170°C)

Alkali source	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT ml
-	86	54	43	29	9	8	8	8	43	32	22	185	13.6 (0.4+3.6)*
3 g Lime	62	38	29	20	7	6	6	7	31	24	14	350	8.0 (0.5+0.5)*

* HPHT filtration at 340 F (170°C), 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

Table n. 15 – Typical Properties of the Fluid Loss Reducer

Property	BF 2745
Chemical description	Polyacrylate ester at high degree of crosslinking in emulsion form
Appearance	Milky emulsion
Brookfield Viscosity	150 cP
Pour Point	< 0°C
Flash Point	> 100°C
Water solubility	Soluble

Table n. 16 – Effect of the FL Reducer in the Mud

Typical Oil/K formate 60/40, ilmenite, S.G. = 2.04; Measurements at 120 F BHR

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	80	48	37	24	7	6	6	6	40	32	16	274
1g BF2745	101	61	47	31	10	8	8	8.5	50.5	40	21	250
4g BF2745	137	92	71	48	16	14	14	15	68.5	45	47	270

Measurements at 120 F AHR 16h at 340 F (170°C)

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT FL* (ml)
-	98	62	49	33	11	9.5	10	10	49	36	26	210	11.6 (0.6+2.4)
1g BF2745	102	68	53	35	12	10	10	11	51	34	34	220	6.8 (0.4+0.6)
4g BF2745	153	122	97	68	24	20	20	21	76.5	31	91	238	3.5 (tr.)

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

Table n. 17 – Effect of the FL Reducer in the Mud

Typical Oil/Cs formate 60/40, ilmenite, S.G. = 2.04; Measurements at 120 F BHR

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
-	60	35	27	18	6	5	5	5	30	25	10	270
1 ppb BF 2745	71	43	32	21	7	6	6	6.5	35.5	28	15	290

Measurements at 120 F AHR 16h at 340 F (170°C)

Fluid loss reducer	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES	HPHT FL* (ml)
-	86	54	43	29	9	8	8	8	43	32	22	185	13.6 (0.4+3.6)*
1 ppb BF 2745	74	47	36	25	8.5	7	7	7.5	37	27	20	270	8.0 (0.2+0.6)*

* HPHT filtration at 340 F (170°C) , 500 psi; the first number in brackets is ml of emulsion and the second is ml of water

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Table n. 18 – Typical Properties of HT Organoclay

Properties	HT Organoclay
Composition	Organically modified hectorite clay
Color	Cream white
Form	Finely divided powder
Specific Gravity	1.7
Moisture	3% Max.

Table n. 19 – Solid Free Emulsions

Measurements at 120 F BHR

Oil / Brine	Brine	S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
50/50	HCOOK	1.2	38	24	19	14	5.5	5	5	7	19	14	10	213
50/50	HCOOCs	1.53	37	24.5	19	14	5.5	5	5	5	18.5	12.5	12	316
40/60	HCOOK	1.26	84	52	41	29	10.5	9	9	9	42	32	20	232
40/60	HCOOCs	1.68	83	52	41	29	10	9	9	9	41.5	31	21	385

Measurements at 120 F AHR 16h at 340 F (170°C)

Oil / Brine	Brine	S.G.	600	300	200	100	6	3	G ₀	G ₁₀	AV	PV	YP	ES
50/50	HCOOK	1.2	38	24.5	19	14	6	5	5	6	19	13.5	11	107
50/50	HCOOCs	1.53	38	25	20	14	6	5	5	5	19	13	12	183
40/60	HCOOK	1.26	82	50	39	27	10.5	9	9	9	41	32	18	93
40/60	HCOOCs	1.68	80	51	40	28	10.5	9.5	9	9	40	29	22	182

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Figure n.1 – Size Distribution of Barite and Ilmenite

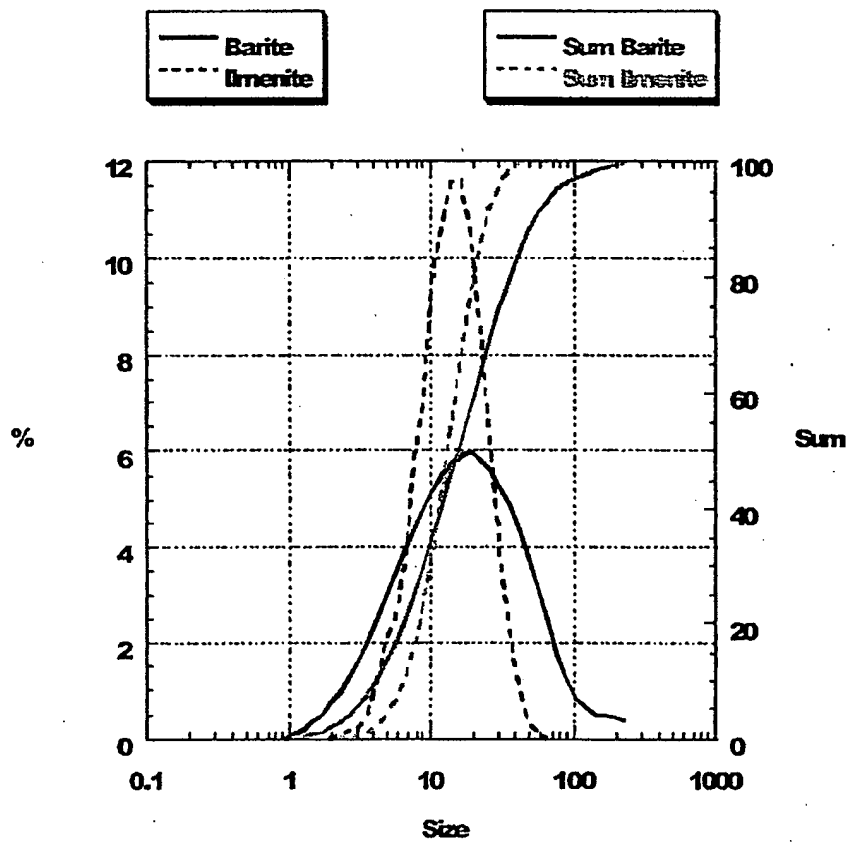
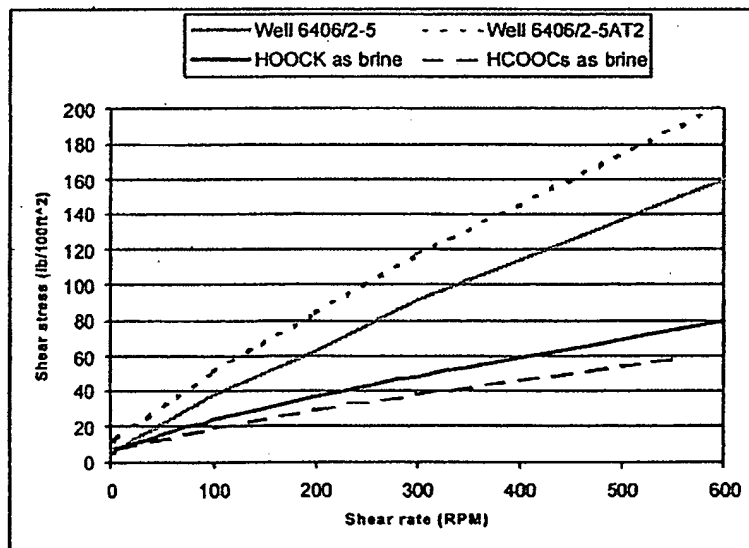
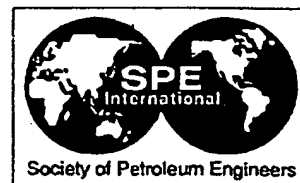


Figure n.2 - Rheological Profile of Kristin Field Mud and New Developed Mud System



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Development Process and Field Applications of a New Ester-based Mud System for ERD Wells on Australia's Northwest Shelf

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Abstract

Extended reach wells drilled from the Goodwyn Alpha platform are highly aggressive and have been drilled with a variety of invert-emulsion mud systems. Historically, mud system selection for these wells was based on compliance to environmental regulations and satisfaction of technical criteria. In order to take a more proactive approach to mud system selection and to raise environmental standards to new levels, an initiative was undertaken to replace the environmentally acceptable, and technically competent mud system being used on Goodwyn with a new ester-based system. Ester-based mud systems are considered the "system-of-choice" in terms of environmental acceptability and possess inherent lubricating qualities for torque and drag reduction.

This paper describes the development process and 4 successful field applications of the new ester-based mud system. A new ester, which exhibits the lowest kinematic viscosity of commercially available esters, was identified and selected for use. New and innovative technologies were introduced in the laboratory development and field applications to address barite sag, hole cleaning efficiency and hydrolytic stability.

The system development and field testing processes were enhanced by daily communication with the development teams in Aberdeen, Houston and Perth. Down-hole friction factors were significantly lower than modeled predictions. Barite sag problems encountered on previous wells were eliminated, and hole cleaning efficiency was optimized.

Introduction

The Goodwyn field is located off the Northwest Shelf of Western Australia. The field was discovered in 1971 by the Goodwyn-1 well, and is one of several large fault blocks located on the Rankin Trend, which form the northern margin of the Dampier sub-basin. The Goodwyn Field Development Plan was written in 1989 to encompass drilling 47 wells: 26 wells from Goodwyn A, 19 wells from a 2nd platform and 2 subsea wells. The plan was to drill the wells at maximum hole angles and horizontal departure of 55° and 4,000 meters, respectively. With the introduction of extended reach drilling, to 7,372 m horizontal step-out, the requirement for the second platform has possibly been eliminated.

The complexity of the Goodwyn extended reach drilling program increased as the wells progressed. The evolution of invert-emulsion fluids used on Goodwyn, from low toxicity oil-based muds (LTBM) to ester-based muds (EBM), had a significant impact on the ability to expand the horizontal reach from the platform and the length of reservoir penetrated. At the conclusion of GWA Phases I & II, a total of 17 wells had been drilled to a maximum step-out of 7,372 m and horizontal section lengths of 2,300 m.

Drilling Fluids

Extended-reach drilling is a form of deviated drilling characterized by lengthy horizontal departures and aggressive hole angles. With consideration to eliminating drilling problems such as excessive torque and drag, poor hole cleaning, stuck pipe, low rates-of-penetration and well-bore stability, increasingly these wells are being drilled with invert-emulsion muds.^{1,2,3}

Invert-emulsion muds have evolved over the past several decades, primarily in response to government-imposed restrictions on the discharge of contaminated cuttings. LTBM were introduced into the UK sector of the North Sea in the early 1980's and the number of wells drilled with LTBM steadily increased in the late 1980's, with growing concern about the impact of discharges on aquatic life.

The industry began searching for alternatives that would provide the drilling performance of LTBM, but without the

associated environmental liability, or HSE impact on rig personnel. Ester-based muds (EBM) were introduced in the early 1990's as a result of this initiative.^{4,5,6} EBM falls into a broad classification of invert-emulsion muds known as synthetic-based muds (SBM), and are classified according to their molecular structure.⁷ Early SBM were made from ester, acetal, ether or polyalphaolefin (PAO) base fluids, followed by internal olefins (IO), linear alpha olefins (LAO) or normal paraffins.

Several types of LTOBM, as well as paraffin and olefin-based SBM, were used in drilling the first 13 wells from the Goodwyn Alpha platform, and proved to be both technically competent and environmentally acceptable. A qualitative study was made of the environmental impact of a number of alternative muds/cuttings management options, including total containment, cuttings injection and the use of water or ester-based muds. Australian regulatory authorities, in line with North Sea equivalents, viewed EBM as a step change improvement on previous systems. In light of the regulatory authority's preference towards EBM, and Woodside's environmental policy, the decision was made to change from a high-performance olefin to an EBM. Additional considerations were:

- Improved economics of EBM (lower cost ester)
- Woodside found it difficult to justify the economics, risks and associated contingency planning for cuttings injection on Goodwyn, given the lack of cuttings injection experience in the area

The risks involved in replacing a technically competent, and environmentally acceptable mud system on these highly aggressive ERD wells were not trivial. It was felt that these risks could be mitigated by developing a new EBM tailored to the wells drilled on the Goodwyn platform.

Development Process

A project was undertaken to develop a new drilling fluid system suitable for drilling challenging ERD wells from the Goodwyn A platform. This system would be recognized as a new "standard" in terms of environmental acceptability on Australia's Northwest Shelf.

Team Communication. The development team was organized from the mud company's Technical Services and Engineering staff in Aberdeen and Houston, respectively. Joint responsibilities were shared by Operations in Perth and team leaders in Aberdeen and Houston. The time allotted to development was only 6 months and, thus required effective teamwork, communication and coordination of efforts across several time-zones to meet the dead-line. The development process was facilitated by frequent input and feedback/review from Woodside. By "inventing-on-schedule" this team developed a new and novel, environmentally safe EBM for use on the Goodwyn platform.

Ester Selection. The first step in the development phase was selection of an ester possessing technical qualities similar to

those of an olefin-based SBM, with the added environmental qualities. Several esters, based on vegetable and fish oil chemistry, were evaluated with consideration to:

- Environmental compliance
- Kinematic viscosity
- Elastomer compatibility
- Lubricity
- Alkaline and temperature stability

Environmental Compliance. Environmental compliance was the most important factor in the ester selection process. In the UK, the toxicity and biodegradability results of the new EBM were sufficient to gain a Category E rating (Table 1), which is the best environmental rating possible with allowance to discharge cuttings.

Kinematic Viscosity. The physical properties of three commercially available esters are shown in Table 2. Kinematic viscosity is an important physical property of base fluids because of its effect on the rheological properties and hydraulics. Fluids with a high kinematic viscosity generally exhibit high plastic viscosity, annular pressure losses and equivalent circulating densities (ECD's).

Kinematic viscosity also has an effect on the volume of ester needed to prepare an EBM system. Brine droplets emulsified into the ester increase plastic viscosity and a balance between volumes of ester and brine must be established. By using an ester with a low kinematic viscosity, higher volumes of brine can be used in formulating a finished barrel of mud. The net effect of this is to reduce mud costs and the environmental impact (from discharges), by reducing the volume of ester in an EBM. From Table 2 one can see that Ester A has the lowest kinematic viscosity of these commercially available esters.

Elastomer Compatibility. Another important performance measure is the compatibility of the ester with oilfield elastomers. Incompatibility between the ester and elastomer can result in changes to the volume and hardness of the elastomer, and subsequent field failures. Table 3 shows the results of elastomer testing in accordance with ASTM D471 and DIN 53521 protocols. These standards describe the requirements for the exposure to fluids and procedures to determine volume changes.

The elastomers tested were less affected by exposure to the n-paraffin and internal olefin-based SBM than to EBM. The esters can be rated in order of reactivity with the elastomers in the following order: Ester B, Ester A and Ester C. Compatibility tests on Ester C were carried out at lower temperature (100 °C), yet it was still the least compatible with elastomers. EBM's formulated with the Ester C have been extensively used with Nitrile elastomers, which suggests that Esters A and C should be equally compatible. In any case, the chosen ester had a damaging effect on some elastomers. This aspect always requires careful testing and monitoring.

Lubricity. As noted by Aarrestad² et al., torque and drag forces are limiting factors in the horizontal displacement of ERD wells. The use of water-based muds in drilling ERD wells is severely restricted because of their generally poor performance in torque and drag reduction. The inherent lubricating qualities of EBM make them ideal for torque and drag reduction in highly aggressive ERD wells.³ A relative comparison of friction coefficients of a high-performance WBM and several SBM is shown in Table 4. The data shows a step-reduction in friction is realized when using conventional SBM in lieu of WBM, with a further reduction occurring with EBM.

Ester Hydrolysis. Esters are susceptible to hydrolysis under conditions of high alkalinity and/or temperature. A low rate of hydrolysis indicates that the ester is chemically stable, which can extend usage in high temperature wells. This is an important consideration when using EBM in wells with high bottom-hole temperatures.

Ester A is produced from the esterification of salmon oil and isopropyl alcohol. Tests were conducted over a range of lime concentrations and temperatures to measure the levels of isopropyl alcohol produced. The amount of isopropyl alcohol liberated was measured by gas chromatography. Alkaline hydrolysis of Ester A begins at concentrations of free lime of 0.5 lbm/bbl (Figure 1). The temperature-induced hydrolysis of Ester A begins at ~ 163 °C (Figure 2).

Distillation. Laboratory tests show that volumes of Ester A cannot be measured directly using a standard 50 ml retort. Distillation tests at different ester-water-ratios were conducted. Comparison of the theoretical and measured test results allowed a correction factor of 1.08 to be established.

Emulsifier Selection. After ester selection, the next phase of the development process centered around the evaluation of surfactant chemistry. Using a novel technique introduced by Quintero⁸ et al., emulsifier efficiency was studied by measuring the size and stability of emulsified droplets using light scattering techniques.

Brine-in-oil emulsions were prepared and evaluated using surfactants, and blends of surfactants, with various hydrophilic/lipophilic (HLB) index values. HLB is related to the size and strength of the hydrophilic (polar) and the lipophilic (non-polar) groups of the surfactant molecule.

The distribution of particle sizes was measured using a Malvern Mastersizer. Droplet size determinations were made initially and after heat aging 16 hours at 121 °C (250 °F). The analyses of results were based on the average droplet size (D[4,3]) and the particle size <90 % (D[0,9]).

Weighting materials were not used during the screening process because of particle size overlap with the brine droplets. All surfactants evaluated formed a stable emulsion of brine in Ester A and the emulsion. The criteria used to evaluate emulsifiers were:

1. Average droplet size of the unweighted emulsion < 10 microns, initially and after heat aging
2. Difference between initial and heat aged average droplet size ± 4 microns
3. HPHT filtration control was used to differentiate from criteria "2" above

Figure 3 shows an example of a poor surfactant for use with Ester A. The shift (increase) in droplet size after heat aging indicates poor emulsion stability. The droplet size distribution of the emulsifier selected for use with Ester A is shown in Figure 4. With this emulsifier the droplet size does not appreciably change after heat aging. The average droplet size is < 5 microns, which is ideal since an average droplet size < 10 microns indicates that optimum emulsion stability.

Additional tests were performed on this emulsifier and appear in Figure 5. After heat aging at 149 °C (300 °F), fluids were left static for a 14-days to allow coalescence of droplets. Using this emulsifier, the average droplet size for the olefin-based SBM varied from 5 to 20 microns, while the EBM ranged from 4 to 8 microns. The emulsifier was previously used in an olefin-based SBM on GWA 13 with good success. These results demonstrate the stability of the EBM emulsion and its resistance to coalescence under static conditions.

Organophilic Clay. Several organophilic clay types and chemistries were evaluated using dynamic oscillatory and traditional oilfield rheological test methodology. From this testing, DFE-434, an ester-specific organophilic clay, was selected for use with Ester A.

Rheological Modifier. Dynamic oscillatory and conventional rheological testing methodologies were also used for screening rheological modifiers. The tests were designed to evaluate the degree to which each additive modified the structure formed by the organophilic clay network. These were balanced against the contribution to viscosity, particularly plastic viscosity, measured with each additive.

DFE-433 was found to be the most effective rheological modifier and also served a secondary function for HPHT filtration control. HPHT filtration rates measured when using DFE-433 were such that further work evaluating HPHT fluid loss additives was not warranted.

Dynamic Oscillatory Tests. Dynamic oscillatory tests provide information about the efficiency of structured fluids that are not apparent in traditional rheological tests.⁹ In these tests the strain response to a sinusoidally varying stress is separated into in-phase and out-of-phase components. Viscoelastic materials exhibit a two component response because some of the energy applied is stored elastically and some is lost. Viscoelastic components are quantified as the elastic or storage modulus (G') and the viscous or loss modulus (G''), and used as sensitive probes of gel structures. The term "storage modulus" is used to describe G' since elastic energy is stored, whereas "loss modulus" is used to describe

G'' since viscous energy is lost. G'' is related to the "liquid-like" characteristics of the material, e.g. the flow behavior of a drilling mud. G' is related to "solid-like" behavior, e.g. how well a drilling mud will suspend solids.

Viscoelastic behavior can be sub-divided into linear and non-linear responses. The most common way of quantifying linear viscoelasticity is through dynamic oscillatory tests. Linear viscoelastic properties are observed when shear stress and strain are proportional. Small deformations are applied to the sample and the viscous and elastic responses are measured. The gel strengths of drilling muds are best measured using small deformations, i.e., through linear viscoelastic tests. Non-linear viscoelasticity implies that shear stress and strain are disproportionate. Large deformations are applied to the sample in non-linear viscoelastic tests. These tests measure the flow behavior of drilling muds, i.e. shear viscosity and shear thinning behavior.

Figures 6 & 7 show the results of dynamic oscillatory tests on a formulation containing DFE-434 and DFE-433. The base mud exhibits the classic profile of a 3-dimensional, linked network, as evidenced by the elastic modulus (G') dominating over the entire frequency region (Figure 6). The gel structure of the base mud exhibits dynamic recovery with time, meaning that the gel recovers after a period of high shear and immediately exhibits elastic behavior (Figure 7).

Optimized EBM System. Several classes of organophilic clays, surfactants and rheological modifiers were evaluated, individually and in combination with one another, in the laboratory development of the new EBM system. Advanced and insightful techniques, such as droplet size measurements and dynamic oscillatory rheological testing were utilized to develop the optimized formulation.

After extensive optimization testing in the Aberdeen and Houston laboratories, two formulations were developed based on satisfaction of the technical specifications listed in Tables 5 & 6. Product concentration studies were carried out for individual, and combinations of products. The primary difference between the formulations was the ester-water-ratio (80/20 and 90/10). The 80/20 EWR formulation was recommended for field testing, with the 90/10 EWR held as a contingency. The 80/20 EWR formulation is simple in that it contains only three components: 1) emulsifier, 2) organophilic clay and 3) dual-function additive for rheological modification and HPHT filtration control.

The rheological and filtration properties of this formulation appear in the form of "wave-curves" in Figures 8 & 9. Wave curves are line-graphs of discontinuous data that would otherwise be presented using bar-charts. The use of "wave-curves" allows one to observe changes in the properties mud from contamination in a single, continuous graph. The profile of the graph was also deemed important and a "flat" rheological profile (stable to contamination) was targeted.

Performance Tests. The 80/20 EWR formulation was subjected to performance tests based upon expected downhole

conditions in the 8 1/2" hole intervals. The mud weight in this section is typically 12.5 lbm/gal and bottom hole temperatures are in excess 112 °C.

Temperature Stability. The effects of temperature on the rheological and filtration properties of this formulation are shown in Figure 10. Plastic viscosity, yield point and HPHT filtration controls values were stable at temperatures up to 150 °C (302 °F). HPHT filtration control increased at temperatures above 165 °C (329 °F).

Static Barite Sag. Static barite sag tests were performed in accordance with the test specifications detailed in Table 5. Tests were performed by placing standard 500 ml heat age cells, at atmospheric pressure, in a static-age oven for 16-hours at 149 °C. The volume of free oil and difference in density of the mud column were measured afterwards. The 80/20 EWR formulation passed both specifications.

An additional test was performed using a modified consistometer, which was pressurized to 10,000 psi. The free oil and static sag values increased in the high pressure test, but were still within the test specifications. Barite sag was monitored during field operations on Goodwyn and none was detected. These results appear in Table 7.

Dynamic Barite Sag. Dynamic barite sag rates were modeled at minimum flow rates and maximum hole angles expected in the 12 1/4" hole interval. Dynamic flow loop tests were performed at a constant annular velocity (AV), for 30 minutes at 65 °C. Static tests were performed for 16-hours at 93 °C. The test results for the optimized 80/20 EWR formulation were:

- Δ Mud Weight at 127 ft/min AV = 0.17 lbm/gal
- Δ Mud Weight at 83 ft/min AV = 0.25 lbm/gal
- Δ Mud Weight at static = 0.78 lbm/gal

Specifications did not exist for dynamic barite sag tests, however, these levels were consistent with results from muds known not to exhibit dynamic barite sag in the field.

Return Permeability. Testing was performed to identify the effects of the new EBM on reservoir production using a Berea sandstone core and Hassler cell permeameter. The results from Table 8 indicate that the wall-cake formed is easily removed from breakout pressures and that the EBM does not impair reservoir production.

HPHT Rheology. Routine rheological tests do not consider the influence of downhole temperatures and pressures on the rheological behavior of the EBM. This is particularly important in ERD wells where hydraulics performance is critical for hole cleaning, ECD, bit and BHA hydraulics.

The Fann® Model 70 viscometer was used to determine the effects of temperature and pressure on the rheological properties of an olefin and the new EBM systems. The

benefits of the optimization work done in the laboratory development of the EBM are apparent from this testing.

Figure 11 shows the effects of temperature (at constant pressure) on the plastic viscosity of an olefin-based and new EBM fluids. While the EBM generally exhibits higher levels of plastic viscosity across the temperature spectrum, they are not proportional to the differences in kinematic viscosity between the olefin and ester base fluids.

Similar comparative testing, showing the influence of increasing temperature on the 6 rpm reading appears in Figure 12. The new EBM exhibits significantly higher 6 rpm readings compared to the olefin-based fluid, which is desirable for aiding hole cleaning efficiency.

Field Applications

A final report detailing the development process and findings was presented to the Goodwyn drilling engineering staff in Perth for approval of a field test.¹⁰ At the conclusion of the presentation, the decision was made to test the new EBM on the Goodwyn Alpha platform. Between October 1998 and August 1999 four extended reach wells (Tables 9-12) were drilled from the Goodwyn A platform using the new ester-based mud system.¹¹

Following Phase I of the Goodwyn drilling program, the "drilling-in-the-box" concept was introduced.¹² This defined a quality wellbore as a section that has been drilled producing a clean smooth wellbore by reducing doglegs, ledges and tortuosity that ultimately reduce the friction factor to allow casing to be run trouble free. The concept was adopted to maximize rates-of-penetration (ROP) while maintaining proper hole cleaning. The ROP envelope was constantly being pushed, with ROP's of 60 m/hr obtained on GWA17 while still maintaining proper hole cleaning.

Milestones from these 4 ERD wells were:

- Successful field introduction of the new EBM
- Woodside's longest ever 13 3/8" casing string run to 3507m (11,506 ft) on GWA14
- Woodside's longest ever 9 5/8" casing string run to 6249m (20,502 ft) on GWA17

GWA 14. The first field trial for the new EBM was in the 12 1/4" hole interval of GWA14. The inevitable teething problems occurred upon initial preparation of the new EBM at the liquid mud plant in Dampier. Viscosity fluctuations were observed in the mud plant, although concentrations were identical to those recommended from laboratory tests. The fluctuations caused great concern because they were unexpected, and could not easily be duplicated in laboratory simulations. Development team members from Aberdeen and Houston worked to resolve the problem and openly communicated findings to the Goodwyn drilling engineering staff.

The new EBM was extremely stable during the 12 1/4" hole interval. HPHT filtration control was easily maintained with minor additions of emulsifier, although filter-cake quality

suffered from the increased levels of low gravity solids. Aggressive centrifuging was required to control the buildup of low gravity solids and maintain stable mud properties.

When running 9 5/8" casing, drag was monitored and plotted using modeling software. Observations from drag modeling and field results indicated that the downhole friction factors were extremely low, and followed a better trend than what was predicted. The actual drag seen (Figure 13) when running casing was lower than expected and almost linear with depth. The cased-hole friction factor (CHFF) was 0.25, with open-hole friction factors (OHFF) averaging 0.2 (Table 11). This was a very successful casing run from a drag reduction point of view.

Innovative technology was utilized to prevent dynamic barite sag at the rig-site using the modern field viscometer shown in Figure 14.^{13,14} This instrument is an improvement over conventional 6-speed viscometers because of several unique features: 1) measuring capabilities at ultra-low shear rates, 2) separation of drive and measuring systems and 3) utilization of a computer acquisition system to record, store and analyze data accuracy.

The "Prevention Window" was developed for use with this viscometer as a tool to predict dynamic barite sag potential. Additionally, the "Prevention Window" optimizes the rheological profile of the fluid and can be used to balance viscosity levels for needed for ECD management and dynamic barite sag prevention. Viscometer data was compared to the limits of the "Prevention Window" and interpreted as follows:

- Viscosity levels below the Lower Limit correspond to a high potential for dynamic barite sag.
- Viscosity levels above the Upper Limit also indicate a low potential for dynamic barite sag, but are excessive in terms of requirements for barite sag prevention.
- Viscosity levels within the limits of the "Prevention Window" are preferred, and indicate a low potential for dynamic barite sag.

Figure 15 shows results taken at a depth of 6144 meters in the 12 1/4" hole on GWA14. The low shear rate viscosity values taken at 49 °C (120 °F) plot at the Upper Limit, indicating a low potential for dynamic barite sag. Barite sag was not observed when running 9 5/8" casing.

The EBM performed well through the course of drilling and logging the 8 1/2" hole section. A large quantity of cement, some of which was "green" or reactive, was drilled and effected the mud system in several ways. First, it was observed that attached to the edges of the bit and stabilizer blades were small particles of a plasticine-type material. It is believed that the combined effects of high bottom-hole temperature and alkalinity arising from drilling reactive cement caused localized hydrolysis of the ester, and formation of these particles. The second effect of drilling reactive cement was to increase HPHT filtration rates. The effects of alkaline conditions could not be clearly delineated because the HPHT test temperature was simultaneously increased from 121 °C to 149 °C in the 8 1/2" hole interval. Treatments were

made to reduce fluid loss with limited success. A supplemental filtration control additive was then used with positive effects on HPHT filtration and filter-cake quality.

The rheological properties of the EBM in this section were stable, even when flowline temperatures rose above 85°C and required continuous additions of water to maintain the ester-water-ratio. There were no serious problems encountered while drilling the 8 1/2" interval and the 7" liner was run and cemented at 7,695 meters.

GWA 15. The 12 1/4" section was drilled without problems in 27 days at a deviation of 86°. This was the second of the Goodwyn wells drilled with the new EBM, and the experience gained on GWA14 identified product concentrations necessary for prevention of barite sag and maintaining efficient hole cleaning. Wellbore integrity was stable even after several weather-related incidents and power failures, during one of which it was not possible to move drill pipe or circulate the mud for 1.25 hours.

Difficulty was seen in measuring the concentration of low gravity solids (LGS) in the mud in the 12 1/4" hole. Error arose in calculating LGS using retort and mass balance methods due to a waxy deposit left in the retort cell. This was compounded by the production of fine, powdered cuttings being generated during periods of sliding. The cyclic degradation of drilled solids to a colloidal particle size effected the rheological properties and drilling hydraulics. Constant centrifugation and dilution were required during intervals of sliding in order to reduce solids levels.

After setting 9 5/8" casing, the EBM on surface was centrifuged to reduce density to 10.8 lbm/gal. The EBM performed well through the course of drilling, logging, and casing the 8 1/2" hole section. Properties were generally very stable and there were no incidences of barite sag and the hole-cleaning efficiency was satisfactory. Hole cleaning efficiency was monitored and graded (1-5 scale) from surface observations of cuttings returned, drag while tripping and torque and drag while drilling. HPHT filtrate was again adversely affected by the initial change to testing at elevated temperature and treatments were made to bring it to within specifications.

GWA16. The 13 3/8" casing was displaced to EBM after drilling the shoe with a 12 1/4" bottom-hole assembly and conducting a formation integrity test (12.9 lbm/gal). The mud generally performed well, with stable mud properties throughout the interval. At TD, the hole was left open 5 days while logging, yet casing was run to bottom with few problems. This was considered a positive reflection on the EBM and on the hole conditions obtained.

The 8 1/2" interval was not a horizontal section, and thus differs from previous sections drilled with the EBM. Water was incorporated into the EBM while running 9 5/8" casing, which affected the EWR and increased rheological properties. Tight hole was encountered in this interval and there was some evidence of sections being over-gauged. The 8 1/2" hole was

plugged and abandoned, resulting in mild cement and spacer contamination to the EBM.

GWA17. The 13 3/8" shoe-track was drilled with the WBM in an attempt to prevent contamination of the EBM with cement. The displacement to EBM on resumption of drilling went well, with a clear interface. The 12 1/4" section was drilled in 10 days with two full trips, one for an MWD failure and the other for a bit change. In addition to these, some precautionary rotary back-washing and wiper trips were performed with a view to keeping the hole as clean as possible for the ambitious 9 5/8" casing run. The entire open hole interval was rotary back-washed and back-reamed before logging. The casing run went extremely well, with no pumping required to work the string down to the desired setting depth of 6,249 meters, although some losses were seen while circulating before cementing.

The rheological properties of the reconditioned mud delivered from the liquid mud plant increased when subjected to downhole shear and temperature, a condition also experienced on GWA 16. These properties were reduced and were fairly stable throughout the interval (Figure 16).

Hole cleaning appeared to be adequate, although 6 rpm readings were generally low. Comparisons of the rheological profile to the "Prevention Window" indicated a low potential for dynamic barite sag, which was confirmed by field observations.

The new EBM exhibited stable rheological and filtration control properties while drilling these 4 ERD wells. Figure 17 shows a several-fold increase in cumulative low gravity solids content of the EBM from GWA14 to GWA17. Over this interval, the percentage of drill solids having a particle size < 2 microns increased from 6 % (GWA 14) to 18 % (GWA17). A comparison of Figures 17 & 18 shows the influence of low gravity solids on plastic viscosity, however the EBM appears resistant to solids contamination and suitable for reconditioning and recycling.

Conclusions

1. A new EBM was "invented-on-schedule" for field testing in the 12 1/4" interval of GWA 14. The development process was facilitated by effective communication and coordination of efforts between the global development teams.
2. New and novel technologies, such as linear viscoelastic rheological and droplet size surfactant measurements, were used to rationalize the development of this system.
3. The system is simple, with robust filtration and rheological control generally achieved with only 3 additives.
4. The new system was instrumental in successfully drilling the 12 1/4" and 8 1/2" hole sections of the Goodwyn Phase II program.
5. Barite sag, hole cleaning or wellbore instability problems were not encountered on the four wells drilled. Innovative field technology was used to monitor the potential for dynamic barite sag.

6. A constant focus on minimizing low gravity solids was required for rheological stability. The inaccuracy inherent of retorting solids made it difficult to quantify the effectiveness of the solids control equipment.
7. The EBM has excellent lubricity characteristics. Open and cased hole friction factors were extremely low.
8. The EBM remained stable throughout the project and was used and reconditioned many times over the 4 wells drilled.

Acknowledgments

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SI Metric Conversions

ft x 3.048 *	E-01 = m
°F (°F-32)/1.8	= °C
lbf/100 ft ² x 4.778 026	E-01 = Pa
lbm/gal x 1.198 264	E+02 = kg/m ³

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Table 1
Environmental Testing – Ester A

Test	Test Protocol	Specification	Result
72 hr EC ₅₀ <i>Skeletonema costatum</i>	ISO/DIS10253	>1000 mg/L	>10,000 mg/L
48 hr LC ₅₀ <i>Arcatia tonsa</i>	ISO T147 5C5 WG2	>1000 mg/L	>1,000 mg/L
10 day LC ₅₀ <i>Corophium volutator</i>		>1,000 mg/Kg	39,737 mg/Kg
28 day Aerobic biodegradation	OECD306	>60%	85 %
60 day Anaerobic biodegradation	ISO CD11734	>60%	>60 %
log Pow	OECD117	N/A	4.99

Table 2
Properties of Esters

Property	Ester A	Ester B	Ester C
Source	Fish Oil	Vegetable Oil	Vegetable Oil
Density (lbm/gal) 20 °C	7.17	7.09	7.17
Kinematic Viscosity, (cSt @ 40 °C)	5.5	8.3	6.0
Flash Point (ASTM D 92, °C)	175	150	179
Cloud Point (°C)	2	< -15	-
Hydrolytic Thermal Stability Limit (°C)	> 175	> 150	-

Table 3
Elastomer Compatibility

Fluid	Elastomer	Temp/72h	Volume Change	ΔHardness	Reactivity
Ester A	D	125 °C	7.9	-6	2
Ester A	F	125 °C	3.8	-2	1
Ester B	D	125 °C	3.4	-1	1
Ester B	F	125 °C	-2	0	1
Ester C	D	100 °C	8.1	-6	2
Ester C	F	100 °C	1.9	-3	1
N-paraffin	D	125 °C	3.9	-4	1
N-paraffin	F	125 °C	0	0	1
Internal Olefin	D	68.3 °C	3.9	-6	1
Internal Olefin	F	150 °C	-0.7	0	1

Elastomer D is Nitrile (NBR) rubber

Elastomer F is Hydrogenated Nitrile (HNBR)

Table 4
Lubricity Tests

Mud System	Coefficient of Friction
PHPA/Glycol WBM	0.28
Mineral Oil	0.20
Internal Olefin	0.19
Ester B	0.16
Ester A	0.15

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Table 5
Drilling Fluid Specifications

Mud Property	Specification
Density (lbm/gal)	12.5
Oil/Water Ratio	80/20 to 90/10
Water Phase Salinity	180 - 200 g/L (23.5 - 25.5% CaCl ₂ Brine)
Plastic Viscosity (cP)	ALAP
Yield Point (lbf/100 ft ²)	<18
Plastic viscosity/yield point ratio	0.8 to 1.5
10 minute Gel (lb/100 ft ²)	<20
Fann 6 rpm reading	12 - 14
HPHT Fluid Loss, ml	<4 (143 °C)
Static Barite Sag, lbm/gal	Δ Mud Weight [(MW top) - (MW bottom)] = <1.46 (143 °C)
Free Oil	<25 ml (143 °C) on base mud

Table 6
Contamination Studies

Contaminant	Specification
Drill Solids	10 % (wt./vol.) or 35 lbm/bbl
Seawater	10 % (vol./vol.) or 35 ml
Barite	Weight up to 2.0 lbm/gal

Table 7
Static Barite Sag

Temperature, °C	Pressure, psi	Free Oil (ml) Specification	Free Oil (ml) Actual	Δ MW Specification	Δ MW Actual
149	14.5	< 25	0.0	<1.46 lbm/gal	0.17 lbm/gal
149	10,000	N/A	3.1	N/A	0.16

Table 8
Return Permeability Testing

Test substrate	Berea Sandstone core
Mud overbalance	500 psi for 2 ½ hours.
Breakout pressure	5.0 psi.
Test Temperature (°C)	65
Return Permeability, %:	100

Table 9
Goodwyn Phase II Wells

Well No	GWA14	GWA15	GWA16	GWA17
Well Type	Producer	Injector	Producer	Producer
TD, meters	7713	6884	6146	6263
Horizontal Displacement, meters	6548	5641	4918	5200
Max Inclination,	96.54°	94.12°	64.78°	70.54°

Table 10
12 ¼" Intervals

Well	GWA14	GWA15	GWA16	GWA17
Well Type	Horizontal	Horizontal	Conventional	Conventional
Inclination	67 - 84°	61 - 86°	61°	67 - 56°
TD, meters	6142	5284	5477	6263

Table 11
9 5/8" Casing & Cementing

Well	GWA14	GWA15	GWA16	GWA17
CHFF	0.25	0.15	0.24	0.20
OHFF	0.1 - 0.3	0.2 - 0.4	0.1 - 0.3	0.1 - 0.4
Planned Time, days	4.7	3.78	4.4	3.86
Actual Time, days	4.7	3.24	3.1	3.19

Table 12
8 1/2" Intervals

Well	GWA14	GWA15	GWA16
Inclination	84 - 96°	86 - 94°	64 - 57°
TD, meters	7713	6884	6146

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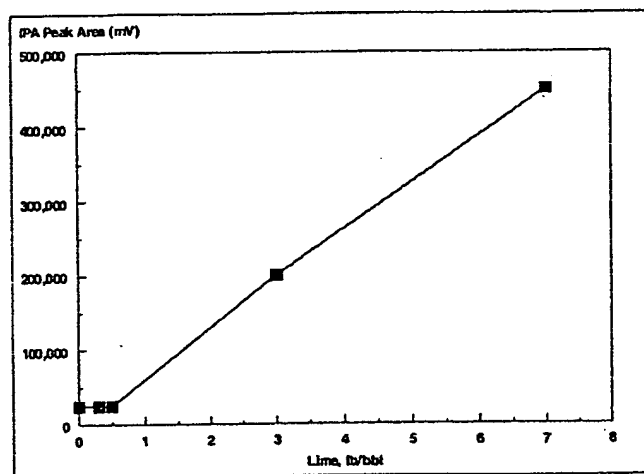


Figure 1 – Alkaline Hydrolysis

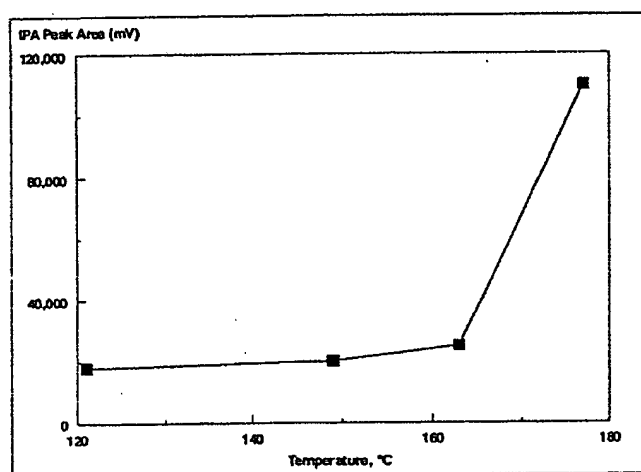


Figure 2 – Temperature Hydrolysis

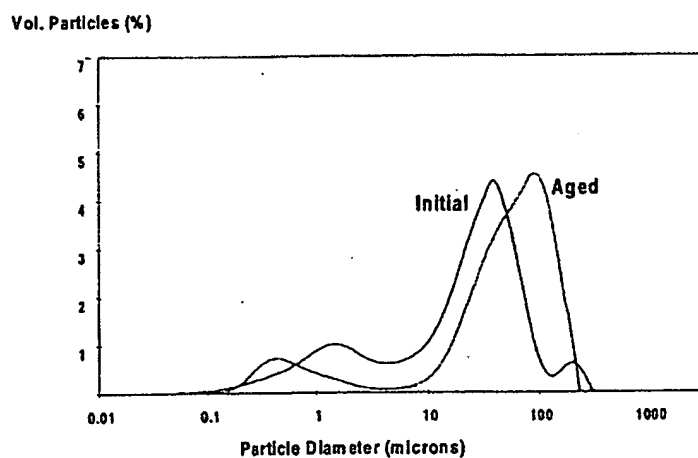


Figure 3 – Droplet Size Measurements – Poor Emulsifier

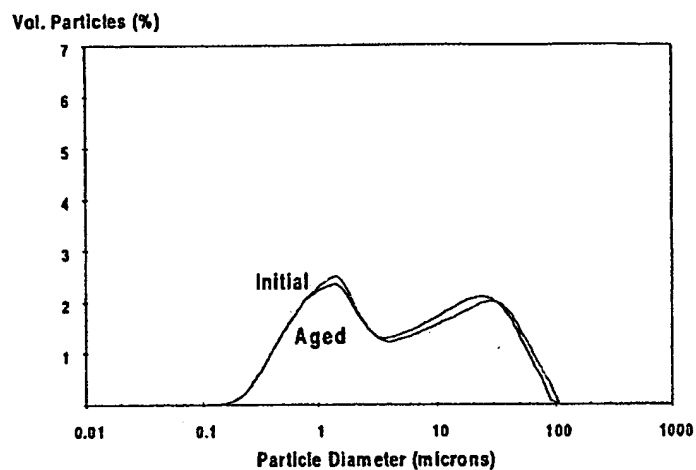


Figure 4 – Droplet Size Measurements – Preferred Emulsifier

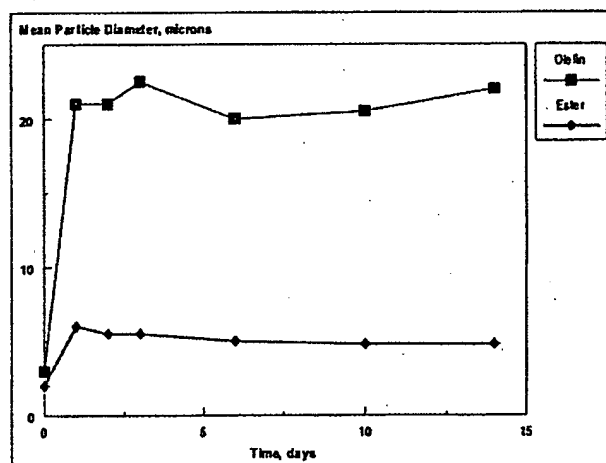


Figure 5 – Droplet Size Stability as Function of Time

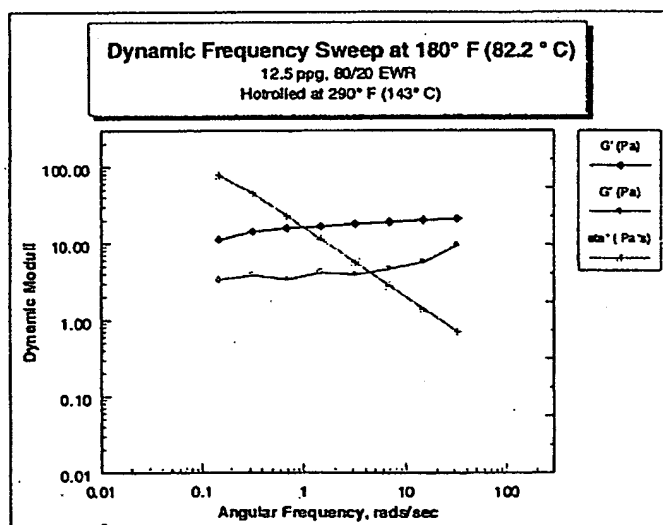


Figure 6 – Dynamic Frequency Sweep

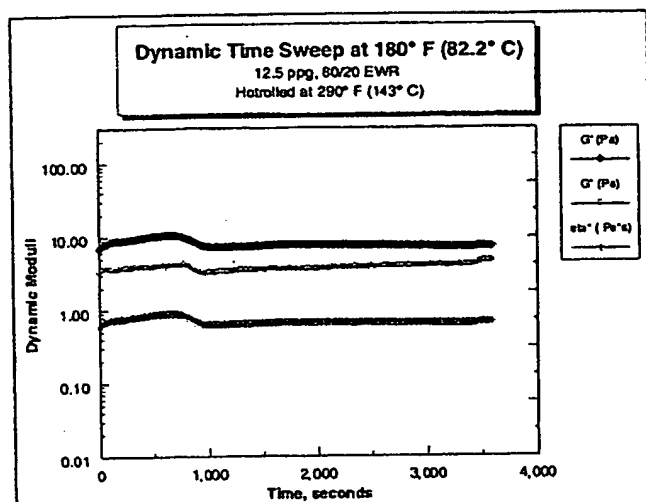


Figure 7 - Dynamic Time Sweep

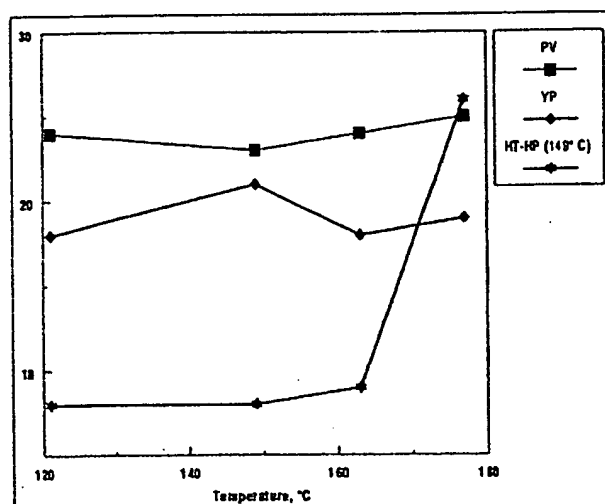


Figure 10 - Effects of Temperature on Properties-80/20 EWR

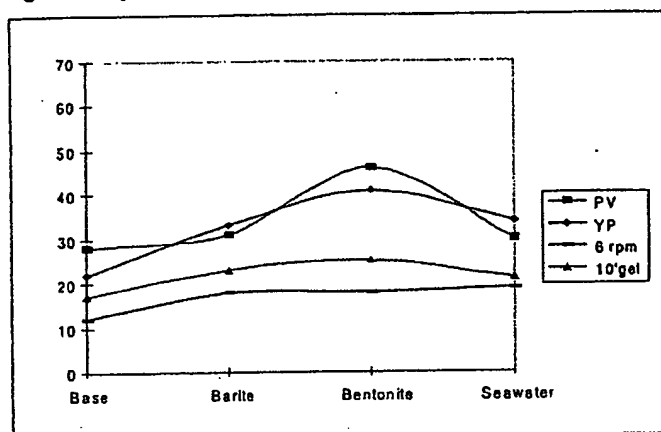


Figure 8 - Wave Curve - 80/20 EWR Formulation (Aged at 300° F)

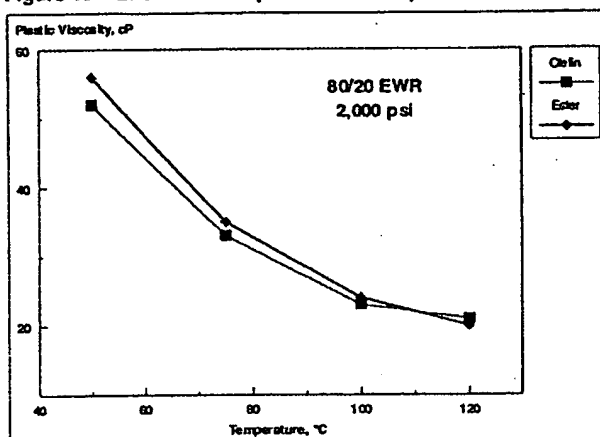


Figure 11 - HPHT Rheology - Plastic Viscosity Comparison

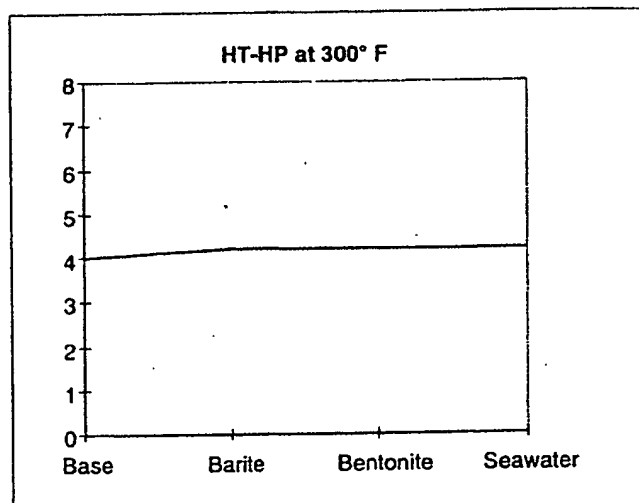


Figure 9 - Wave Curve - 80/20 EWR Formulation (Aged at 300° F)

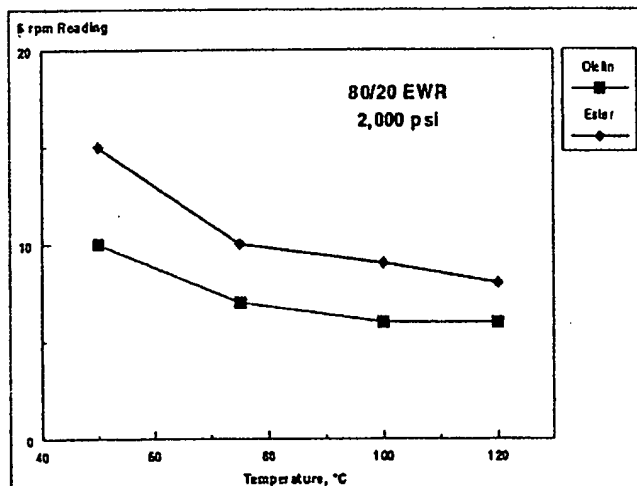


Figure 12- HPHT Rheology - 6 rpm Reading Comparison

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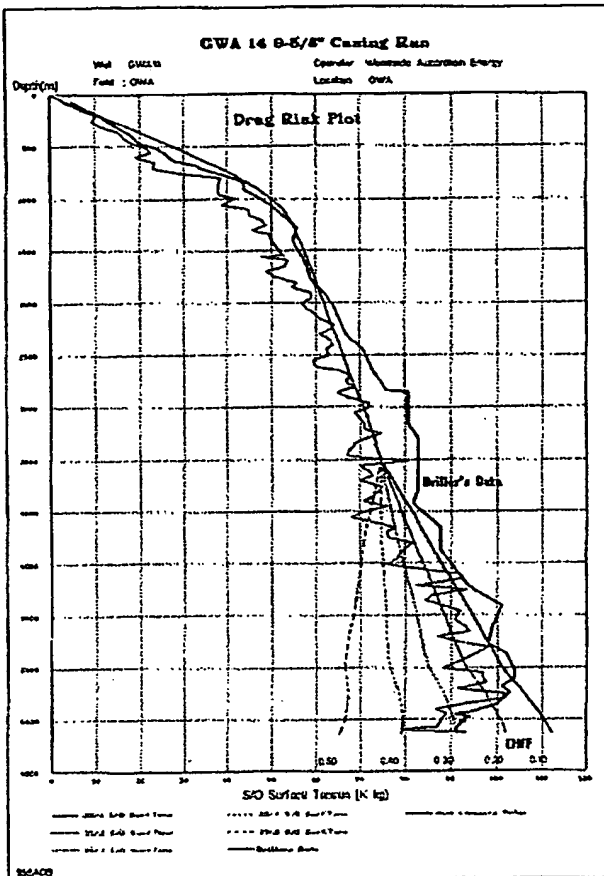


Figure 13 – Drag Plot GWA14, 9 5/8" Casing at 6144 meters

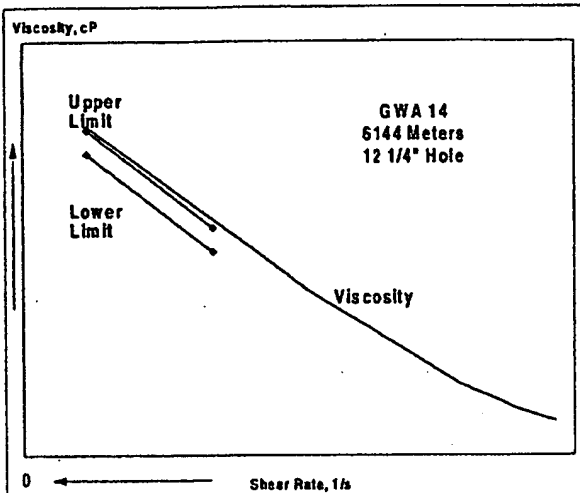


Figure 15 – Barfite Sag “Prevention Window” GWA14

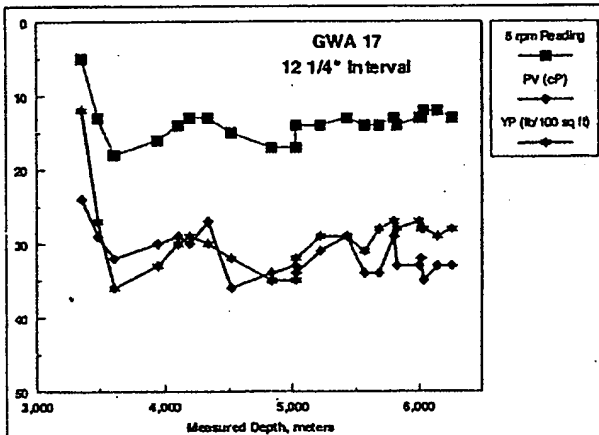


Figure 16 – EBM Properties in 12 ¼" Hole – GWA 17

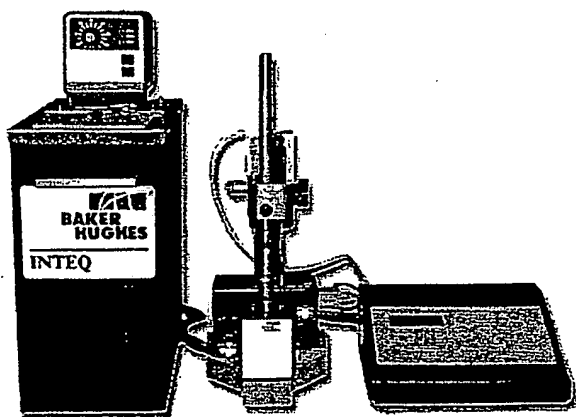


Figure 14 – Rig-site Viscometer

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GWA-14/15/16/17 LGS kg/m³

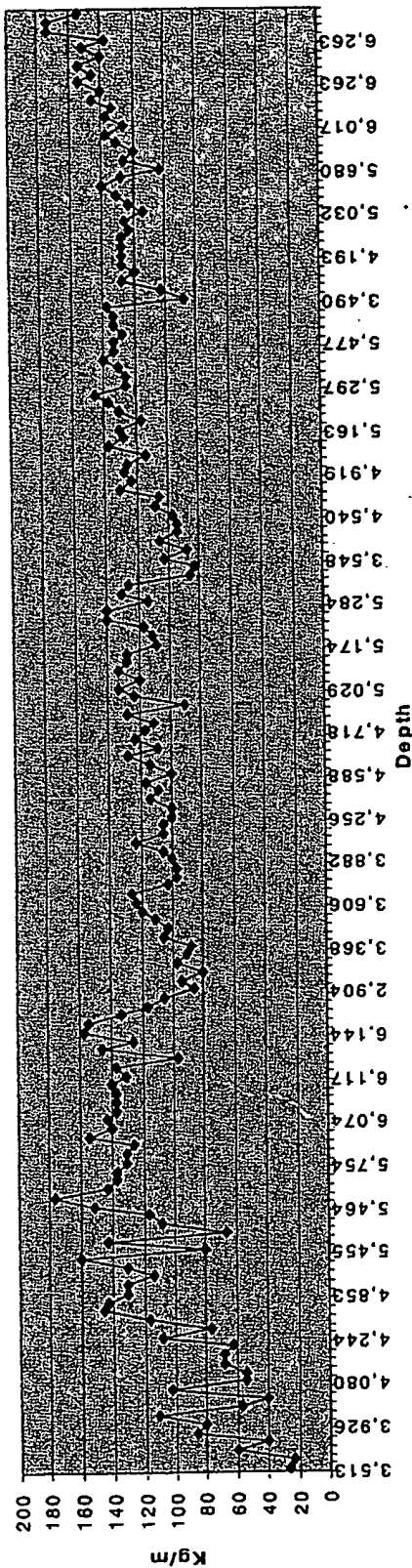


Figure 17 - Cumulative Increase in Drill Solids- 12 1/2" Intervals

GWA-14/15/16/17 PV cP @ 86C

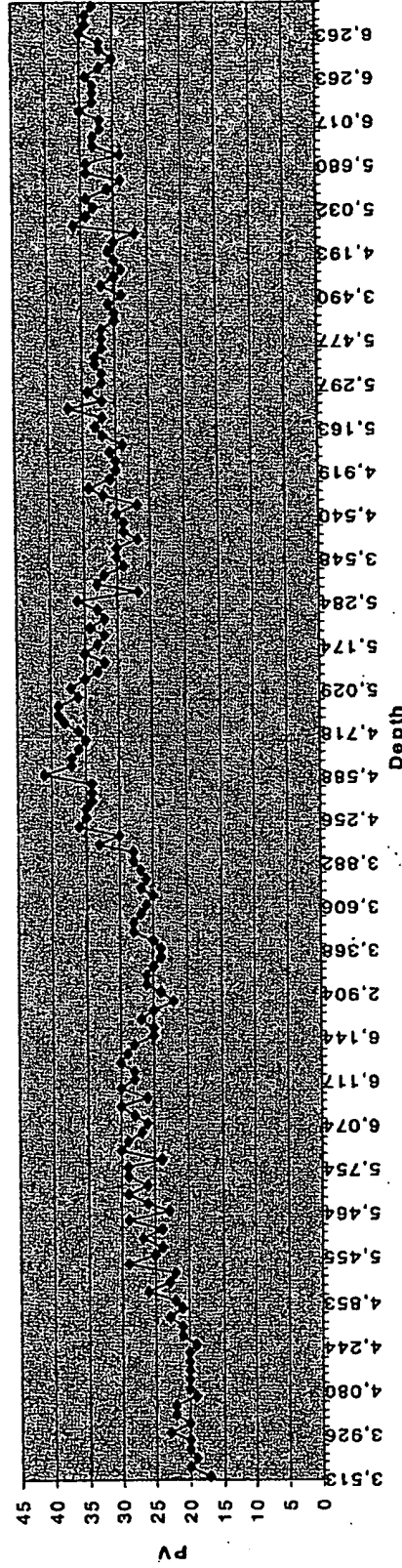


Figure 18 - Cumulative Increase in Plastic Viscosity- 12 1/2" Intervals



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MIPI 000184

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GA	Gabon			VN	Viet Nam

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BASE OIL FOR WELL-BORE FLUIDS

The present invention relates to base oils for use in well-bore fluids, such as drilling fluids, to well-bore fluids incorporating the base oil and to the use of such fluids.

5 Well-bore fluids, for example drilling fluids, are used in oil and gas recovery and in geothermal energy and mineral exploration and extraction operations. The fluid serves a number a functions including removal of drilled cuttings from the bore-hole and sealing of the well-bore surfaces so that fluid loss into the formation being drilled is minimised. The fluid also lubricates and cools the drill pipe during the
10 drilling operation.

Oil based drilling fluids have been used for around 50 years for drilling underground formations to recover oil and gas. Oil based fluids are preferred systems compared with water-based formulations, especially where highly water-sensitive underground formations are being drilled. In water-based fluids water tends
15 to migrate from the fluid to the formation being drilled. This destabilizes the formation and can lead to disintegration and breakdown of the bore-hole. Furthermore, water-based fluids tend to be unsuitable for use at high temperatures and where highly deviated bore-holes may be required to reach the targeted formations.

20 In view of the disadvantages of water-based fluids the recent trend has been to use drilling fluids which are oil-based. However, oil-based fluids previously used containing base oils such as diesel and crude oil, are toxic and only slightly biodegradable. This is obviously unsatisfactory with respect to environmental health and safety considerations, especially as drill cuttings coated with or containing the
25 fluid are usually discharged to the sea floor when drilling off-shore. The use of these kinds of oil-based fluids can have a detrimental effect on marine organisms.

It has been proposed to use mineral oils as the base oil in drilling fluids instead of other petroleum derived oils. However, while less toxic than these other petroleum based drilling fluids mineral oil based fluids are not very biodegradable.
30 Surveys on drill cuttings on the seabed of the North Sea have confirmed the persistence of mineral oils.

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More recently attention has focused on the use of esters, ethers and white oils as base oils. These have improved toxicity characteristics, approaching that of water, and have reasonably good aerobic biodegradability. However, with the exception of the esters they typically exhibit poor anaerobic biodegradation. Anaerobic
5 biodegradation is required, for example, at the sea floor. Also, these base oils tend to have high kinematic viscosities and temperature limitations. Furthermore, with the exception of the white oils they are very expensive when compared to the kinds of mineral oils described above.

The present invention seeks to provide a base oil for use in oil-based well-bore
10 fluids, such as drilling fluids, which overcomes the disadvantages discussed above. In particular, the present invention seeks to provide a base oil which has low toxicity, good aerobic and anaerobic biodegradability and a combination of physical characteristics which are especially well suited to its use as a well-bore fluid. It is also an object of the invention to provide a base oil which is inexpensive.

15 Accordingly, the present invention resides in the use as base oil in a well-bore fluid of a mixture comprising at least 70% by weight of one or more normal alkanes having from 11 to 16 carbon atoms, wherein the mixture has a pour point of less than -2°C.

The mixture typically comprises 30% by weight, or less, of one or more
20 branched or cyclic alkanes having from 11 to 16 carbon atoms.

As it is extremely important that the base oil biodegrade as quickly as possible it is preferred that the mixture comprises a very high proportion of normal (straight chain) alkanes. Branched-chain and cyclic hydrocarbons are not broken down by bacteria as rapidly as normal hydrocarbons. According to a preferred embodiment
25 of the invention the mixture comprises at least 90% by weight of the one or more normal alkanes. More preferably the mixture comprises at least about 98% by weight of the one or more normal alkanes. Mixtures of normal alkanes having from 11 to 16 carbon atoms are most preferably used.

The toxicity to flora and fauna of base oils used in drilling fluids is believed
30 to be directly linked to aromatic content. To minimise toxicity therefore the aromatic

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content in the mixture must be kept as low as possible, 0.1% by weight being the typical maximum allowed.

The pour point of drilling fluids is a particularly important characteristic as it is essential that the fluid is capable of being pumped at the lowest temperature encountered during mixing, storage, transportation and use. The pour point of the fluid is primarily influenced by the pour point of the base oil which is used.

In PCT patent application WO 95/06694, published on March 9, 1995, there is an indication on its page 4, lines 12-16, that when using normal alkanes as a drilling fluid in a cold environment, one may use a pour point depressant to reduce the pour point (freezing point) of the fluid.

In accordance with the present invention the base oil mixture has a pour point of less than -2°C , preferably -9°C or less. However, these represent the pour point of the mixture without the addition of pour point depressants. Pour point depressants could be used but they tend to be of little effect in pure normal alkane mixtures. The addition of pour point depressants may in fact lead to undesirable side-effects such as increased toxicity and low flash point. Pour point depressants may also cause decreased stability of invert emulsion well-bore fluids.

To minimise or prevent the danger of fire or explosion of oil-based drilling fluids the base oil used should have a flash point which is higher than the surface circulating temperature of the fluid during drilling of the well-bore. Preferably, the base oil used in the present invention has a flash point of at least 65°C , more preferably at least 80°C .

A further important characteristic of the base oil used is its kinematic viscosity. This is crucial to the ability of the drilling fluid to tolerate solids and water, whether added as integral components or accumulated during the mechanism of drilling into formations or by formation water intrusion. Generally, the lower the kinematic viscosity of the base oil used the higher the tolerance of the fluid is. Through practical experience it has been found that the base oil should preferably have a kinematic viscosity of from 1 to 10 cSt, more preferably from 1 to 6 cSt, at 40°C , and this is a feature of the base oil of the present invention. Base oils having a viscosity of about 1 cSt at 40°C are believed to be the most tolerant to solids and

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water. Difficulty in pumping tends to be encountered when using base oils having a viscosity at 40°C of greater than 6 cSt.

Base oils which may be used in the present invention are commercially available, and tend to be produced through cracking, reaction and distillation processes.

The present invention also provides a well-bore fluid comprising as base oil the mixture as described above in combination with an emulsifier, oil-wetting agent, viscosifier, filtration control additive, rheology modifier, thinner and/or weighting agent. These are additives conventionally used in well-bore fluids and the combination which is used depends upon the desired characteristics of the fluid being formulated.

Emulsifiers which may be used include fatty acids, soaps of fatty acids and fatty acid derivatives and amidoamines, polyamides, polyamines, esters such as sorbitan monoleate polyethoxylate and sorbitan dioleate polyethoxylate, imidaxolines and alcohols.

Typical oil wetting agents which may be used include lecithin, fatty acids, crude tall oil, oxidized crude tall oil, organic phosphate esters, imidazolines, amidoamines, alkyl aromatic sulphates, alkyl aromatic sulphonates, and organic esters of polyhydric alcohols.

Typical viscosifiers include organophilic clays (eg. hectorite, bentonite and attapulgite), oil soluble polymers and resins, and polymers such as sulphonated ethylene propylene diene (EPDM) terpolymers and sulphonated butadiene styrene copolymers.

As filtration control additives which may be used there may be mentioned asphalt and derivatives thereof, gilsonite, amine-treated lignite and polymers such as EPDM terpolymers, styrene butadiene copolymers and acrylate styrene copolymers.

Typical rheology modifiers include fatty acids and polymeric fatty acids.

Thinners which may be used include petroleum sulphonates, amidoamines, alkaryl sulphonates and polyamines.

Examples of weighting agents include barite, iron oxide, iron carbonate, calcium carbonate and galena.

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It is possible to use the base oils alone, i.e. without the use of the conventional additives described. Typically, however additives are required to tailor the properties of the fluid to meet specific requirements.

5 The well-bore fluid may be an all oil-based fluid or an invert emulsion (i.e. a water-in-oil emulsion) formed using water, brine or a polar organic liquid which is insoluble in the base oil. Preferably, the polar organic liquid is glycerol, methanol or propylene carbonate. When the well-bore fluid is an invert emulsion, the emulsified phase typically represents from 1 to 70% by volume of the fluid.

10 The use of fluid which is an invert emulsion enables the overall cost to be reduced by reducing the volume of base oil needed. The water activity of the invert emulsion can be adjusted by the addition of inorganic salts to balance the water activity of the formulation being drilled into. Examples of inorganic salts which may be used include the sodium, potassium, calcium, magnesium, caesium and zinc chlorides, sodium, calcium and zinc bromides, sodium, potassium and caesium
15 formates, sodium and potassium acetates and calcium and ammonium nitrates.

The typical proportions of these additives in the well-bore fluids of the present invention are shown in the following table.

	<u>Typical</u>	<u>More Typical</u>
Base oil, Volume %	20-100	50-90
20 Emulsifier, lb/bbl	1-20	4-16
Oil wetting agent, lb/bbl	0-10	0.5-4
Viscosifier, lb/bbl	0-15	1-6
Filtration control additive, lb/bbl	0.5-25	1-10
Rheology modifier, lb/bbl	0-4	0.5-2
25 Thinner, lb/bbl	0-10	0.5-4
Weighting agent, lb/bbl	0-700	0-500
Water, Volume %	0-60	20-50
Calcium Chloride, lb/bbl	0-150	2-100
(to adjust water activity)		

30 In this table lb/bbl represents pounds per US barrel. The well-bore fluids of the present invention are prepared by conventional techniques by mixing of the

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constituents. Preparation of the oil-based drilling fluid may take place at a land-based mud-mixing facility, or at the well-site. Mixing typically takes place in tanks equipped with circulating centrifugal pumps and agitation/shear equipment.

5 Although primarily described as a drilling fluid, the base oil described is suitable for use generally as a well-bore fluid. The base oil can be used for example as a pay zone drill in fluid, a completion fluid, a "kill" fluid, a packer fluid or casing pack, a "spotting" fluid or a "spacer".

The invention further provides a method of drilling using a well-bore fluid of the invention as described above.

10 The following Examples illustrate the present invention. Unless otherwise states US gallons and barrels are referred to herein.

Example 1

15 A laboratory barrel (350ml) of drilling fluid was prepared by mixing the various ingredients shown in the table below using a Silverson mixer at a speed of 6,000 rpm using a square hole disintegrator head. The total mixing time was 1 hour and the ingredients were added in the order listed, a period of five minutes being allowed between each ingredient addition. A water bath was used to maintain the temperature below 65°C (150°F).

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TABLE 1

	Ingredient	Amount	Function
	Base oil A	136 ml	Base oil
	EZ MUL 2F'	10 g	Emulsifier
5	GELTONE II'	2.5 g	Viscosifier
	Lime	4 g	Alkalinity Control
	DURATONE HT'	4 g	Filtration Control
	Freshwater	136 ml	Emulsified Phase
	Barite	163 g	Weighting Agent
10	Calcium Chloride (82% pure)	60 g	Water Activity Balance
	RM-63'	1 g	Rheology Modifier

' - available from Baroid Limited

The fluid formed has the following properties:

15	Density	:	1.38kg/m ³ (11.5lb/gal)
	Oil/Water Ratio	:	50/50
	Water Phase Salinity	:	250,000 ppm calcium chloride

Base oil A has the following composition and properties:

		wt %
20	n-C ₁₁	9.1
	n-C ₁₂	21.7
	n-C ₁₃	36.2
	n-C ₁₄	31.3
	n-C ₁₅	1.4
25	n-C ₁₆	0.04
	> C ₁₆	trace
	aromatics	<0.1

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Pour point	= -9°C
Flash point	= 91°C
Kinematic Viscosity at 40°C	= 1.75cSt

The properties of base oil A compared with some commercially available
5 North Sea base oils is illustrated in Table 2 below.

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TABLE 2

Base Oil	Density g/ml @ 15°C	Flash Point °C (PMCC)	Aromatics % (Max)	Aniline Point °C	Kln. Viscosity cst at 40°C	Pour Point °C
Test Procedure	ASTM D129	ASTM D93	ASTM D2887	ASTM D611	ASTM D445	ASTM D97
Base Oil A	0.759	91	0.1	93	1.75	-9
BP 83 HF	0.790	95	4.5	88	2.40	-10
Fina DMF 120	0.820	74	2.3	73	1.72	nd
Fina DMF HF	0.820	103	3.9	82	2.90	-18
Total DF1	0.800	77	0.5	77	1.73	-39
Total HDF	0.814	100	6.0	86	3.20	-30
Shellsol D90	0.805	95	0.1	78	2.00	-20
Shellsol D70	0.792	72	0.5	78	1.62	-30
Clairsol 350	0.798	78	4.1	76	1.89	-35
Clairsol 450	0.815	93	4.4	88	3.40	-20
Clairsol 350MHF	0.783	94	2.0	78	2.20	-20
PETROFREE	0.860	179	0.0	na	6.00	-30

nd - not determined
na - not applicable

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It can be seen from this table that base oil A compares very favourably with the other oils which are used to formulate well-bore fluids with respect to the combination of characteristics it possesses.

Example 2

- 5 The properties of a laboratory barrel (350ml) of the fluid of Example 1 were measured in accordance with API RP 13B-2. The properties of the fluid were also measured when contaminated with 35g Hymod clay, 10% by volume seawater and 10% by volume carnalite brine. The results are shown in Table 3 below.

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TABLE 3

MEASURED PROPERTIES						
	Fluid of invention		Fluid + Hymod Clay	Fluid + Seawater	Fluid + Carnalite Brine	
Hot Rolled (250°F) hours	-	16	16	16	16	
Fann 35 Readings at 120°F:						
600 rpm	85	101	159	118	96	
300 rpm	55	61	104	72	59	
200 rpm	43	45	85	54	45	
100 rpm	33	30	61	35	30	
6 rpm	16	13	26	14	11	
3 rpm	14	12	24	13	10	
Plastic Viscosity, cp	28	40	55	46	37	
Yield Point, lb/100ft ²	27	21	49	26	22	
10 sec Gel, lb/100ft ²	14	13	30	13	9	
10 min Gel, lb/100ft ²	20	20	40	20	10	
Electrical Stability V	288	345	209	122	130	
HPHT Filtrate, at 250°F, ml	-	2.8	3.0	3.6	3.2	

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This table shows that the well-bore fluid of the invention is very stable to contaminants. It should be noted that the well-bore fluid exhibits very good, low rheological properties even though the water content of the fluid is 50% by volume. This shows how the low kinematic viscosity of the n-alkane mixture base oil contributes to the ability of the fluid to tolerate high added concentrations of water, and water as a contaminant.

Example 3

Following the same procedure as Example 1 a laboratory barrel (350ml) of well-bore fluid was prepared. The ingredients were mixed in the order listed in Table 4 below. Base oil A was the same as that used in Example 1.

TABLE 4

Ingredient	Amount	Function
Base Oil A	147 ml	Base oil
EZ MUL 2F ¹	20 g	Emulsifier
DURATONE HT ¹	11 g	Filtration Control
XP-10 ¹ (Experimental product)	3.5 g	Filtration Control
BENTONE 38 ²	0.5 g	Viscosifier
SUSPENTONE ¹	4 g	Viscosifer
Lime	4 g	Alkalinity Control
Freshwater	28 ml	Emulsified Phase
Barite	589 g	Weighting Agent
Calcium Chloride (82% pure)	9.7 g	Water Activity Balance
RM-63 ¹	0.75 g	Rheology Modifier

¹ - available from Bariod Limited

² - available from Rheox

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The fluid formed has the following properties:

Density	: 2.24kg/m ³ (18.67 lb/gal)
Oil/Water Ratio	: 85/15
Water Phase Salinity	: 250,000 mg/L calcium chloride

5 **EXAMPLE 4**

Example 2 was repeated using a laboratory barrel of the well-bore fluid of Example 3. The contaminants used were Hymod clay (35g) and seawater (10% by volume). The fluid was hot rolled at the temperatures shown in Table 5 below. This table shows the properties of the fluid.

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TABLE 5

MEASURED PROPERTIES									
	Fluid of the Invention				Fluid + Hymod Clay		Fluid + Seawater		
Hot Rolled (350°F)	hours	-	16	-	-	-	-	-	-
Hot Rolled (395°F)	hours	-	-	16	-	16	-	16	-
Static Aged (395°F)	hours	-	-	-	16	-	-	16	16
600/300	rpm	130/75	132/78	131/74	165/98	182/111	183/120	136/85	168/109
200/100	rpm	58/38	61/40	58/37	74/48	88/62	97/68	67/27	87/61
6/3	rpm	12/10	16/14	14/12	17/15	28/27	28/24	16/14	24/20
Plastic Viscosity	cp	55	54	57	67	71	63	51	59
Yield Point	lb/100ft ²	20	24	17	31	40	57	34	50
10 sec Gel	lb/100ft ²	12	16	22	18	26	28	22	23
10 min Gel	lb/100ft ²	21	21	24	26	32	36	25	28
Electrical Stability	V	1393	1218	1484	1002	1215	1560	713	1211
HTHP fluid loss, ml @ 395°F			5.4	5.8	11.2	8.2	14.0	6.4	12.0

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The results confirm the stability of the fluids of the invention even when exposed at high temperature to contaminants.

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What is claimed is:

1. A base oil for use in a well-bore fluid of a mixture comprising at least 70% by weight of one or more normal alkanes having from 11 to 16 carbon atoms, with no more than a trace of said normal alkanes having greater than 16 carbon atoms, wherein the mixture has a pour point of less than -2°C without containing a pour point depressant.
2. The base oil according to Claim 1, wherein the mixture comprises up to 0.1% by weight aromatics.
3. The base oil according to Claims 1 or 2, wherein the mixture comprises 30% by weight, or less, of one or more branched or cyclic alkanes having from 11 to 16 carbon atoms.
4. The base oil according to any one of Claims 1 to 3, wherein the mixture comprises at least 90% by weight of one or more normal alkanes.
5. The base oil according to Claim 4, wherein the mixture comprises at least about 98% by weight of one or more normal alkanes.
6. The base oil according to any one of the preceding claims, wherein the mixture has a pour point of -9°C or less.
7. The base oil according to any one of the preceding claims, wherein the mixture has a flash point of at least 65°C.
8. The base oil according to Claim 7, wherein the mixture has a flash point of at least 80°C.
9. The base oil according to any of the preceding claims, wherein the mixture has a kinematic viscosity at 40°C of from 1 to 10 cSt.
10. The base oil according to Claim 9, wherein the mixture has a kinematic viscosity at 40°C of from 1 to 6 cSt.
11. A well-bore fluid comprising as base oil a mixture as defined in any one of Claims 1 to 10 in combination with one or more of an emulsifier, oil-wetting agent, viscosifier, filtration control additive, rheology modifier thinner, weighting agent and/or other well-bore fluid additive.
12. A fluid according to Claim 11 comprising from 20% to 100% by weight of base oil mixture, based on the total weight of the fluid.

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13. A fluid according to Claims 11 or 12 which is an all oil-based fluid.
14. A fluid according to Claims 11 or 12 which is an invert emulsion with water, brine or a polar organic liquid which is insoluble in the base oil mixture.
15. A fluid according to Claim 14, wherein the polar organic liquid is
5 glycerol, methanol or propylene carbonate.
16. A method of drilling a well which comprises using as drilling fluid the drilling fluid defined in any one of Claims 11 to 15.

MIPI 000203

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/00993

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 585/1,2; 507/100,103,110,111,116,117,118,119

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/1,2; 507/100,103,110,111,116,117,118,119

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A, 8302949; (Jachnik); 01 September 1983; see page 7, lines 3-4 and 21-34 and page 10, lines 4-10.	1-3
X	WO, A 95 006694 (Sawdon); 09 March 1995; see page 2, lines 21-25, column 6, lines 5-18.	1-3
-,P		---
Y		1-3
Y	US,A 4,508,628 (Walker et al); 02 April 1985; see column 4, lines 45-59.	1-3
Y	US,A, 5,333,698 (Van Slyke); 02 August 1994; see column 2, lines 10-24.	1-3

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

18 APRIL 1996

Date of mailing of the international search report

14 MAY 1996

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Form PCT/ISA/210 (second sheet)(July 1992)*

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MIPI 000204

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/00993

Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(Z)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4-16
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
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Form PCT/ISA/210 (continuation of first sheet(1))(July 1992)*

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International application No.

PCT/US96/00993

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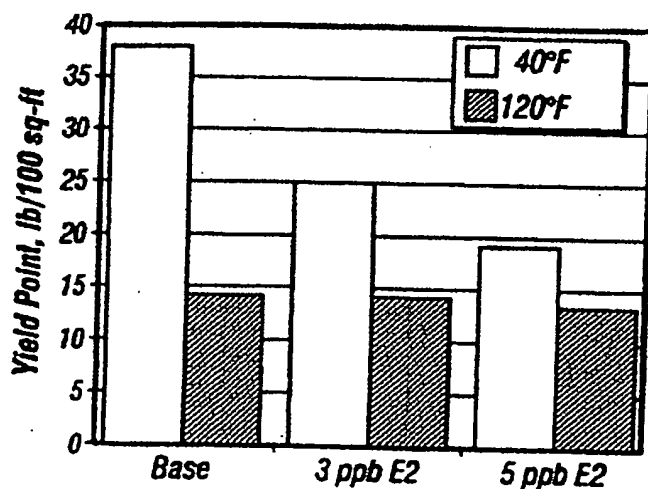
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Published:

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: THINNERS FOR INVERT EMULSIONS



(57) Abstract: A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said drilling fluids or well service fluids a thinner having the formula: $R-(C_2H_5O)_n(C_3H_7O)_m(C_4H_9O)_k-H$ where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) HALB-016

Box No. I TITLE OF INVENTION
THINNERS FOR INVERT EMULSIONS

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Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this box is the applicant's State (that is, country) of residence (if no State of residence is indicated below.)

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THINNERS FOR INVERT EMULSIONS

Background of the Invention

1. Field of the Invention

5 This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids, at temperatures at or below about 50 degrees
10 Fahrenheit (about 10 degrees Centigrade).

2. Description of Relevant Art

 A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid
15 include removing drill cuttings from the wellbore, cooling and lubricating the drill bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

20 A drilling fluid typically comprises water and/or oil or synthetic oil or other synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in
25 the fluid. Such dispersed water in oil is generally referred to as an invert emulsion or water-in-oil emulsion.

 A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or
30 fluid-loss control agents, viscosifiers or viscosity control agents, and alkali. Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

5 An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling operation. Moreover, a drilling fluid must be sufficiently viscous to be able to suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

10 Thinner may be added to the drilling fluid or drilling mud systems before and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, problems with such prior art thinners may occur when using the drilling muds at low temperatures (temperatures at or below about 50°F (10° C)).

20 At such low temperatures, despite the use of known prior art thinners, oil based drilling fluids typically have high or increased viscosity, which may render the fluids unusable for drilling. After pumping into the wellbore, drilling fluids may undergo heating from the formation, depending on the depth of the wellbore and the temperature of the formation. For example, heating in the range of about 150° to about 250°F (about 66° to about 121°C) is not uncommon and subterranean temperatures as high as about 350°F (about 178°C), particularly in very deep wellbores, are known. The Arctic region, for example, is known to have very low surface temperatures but very high subterranean temperatures. Even more problematic are deepwater wells (i.e., typically wells below at least about 1500 feet), which subject drilling fluids to chilling from cold waters surrounding the riser as the fluid returns to the surface from the high temperature subterranean formation. Such chilling of oil

based drilling fluids typically increases their viscosity while such subterranean heating of oil based drilling fluids typically reduces their viscosity.

Preferably, thinners which reduce the viscosity of drilling fluids at low temperatures will not affect the viscosity of the fluids at high temperatures.

5 That is, in many cases, a thinner is desired that is capable of "selectively" influencing the rheology or particularly reducing the viscosity of oil-based drilling fluids only at lower temperatures, such as may be encountered at the ground surface of the wellbore, or in the riser surrounded by waters above a deepwater offshore well, for example.

10 Thinner and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further, drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore,
15 such as high temperatures, high pressures, and pH changes.

A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising invert (water-in-oil) emulsions, which are expected to be used in or to encounter low temperatures in drilling operations. As used herein, unless
20 indicated otherwise, "low temperatures" shall be understood to mean temperatures at or below about 50°F (about 10°C).

Summary of the Invention

According to the method of the present invention, a compound is added
25 to a water-in-oil or invert emulsion drilling fluid or well service fluid which reduces the viscosity of the drilling fluid or well service fluid at low temperatures or which enables or enhances the ability of the drilling fluid or well service fluid to maintain its viscosity at low temperatures. The compound, which may be generally called a "thinner," continues to have this effect on a drilling fluid or
30 well service fluid in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations. Further, this compound does not significantly affect the viscosity of the emulsion at high temperatures.

The compound has the following formula:



- 5 where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

10 The invention also comprises the composition of a water-in-oil or invert emulsion drilling fluid or well service fluid containing this thinner compound.

Brief Description of the Drawings

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2 at different
15 temperatures.

Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3 at different temperatures.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4 at different
20 temperatures.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5 at different temperatures.

25 Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6 at different temperatures.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7 at different
30 temperatures.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8 at different temperatures.

Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9 at different temperatures.

5 Detailed Description of Preferred Embodiments

The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of drilling fluids or well service fluids comprising invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing
10 subterranean formations and has particular advantage in applications where the fluids are subjected to low temperatures, as in drilling or in servicing deepwater offshore wells. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and
15 various additives. As the term is used herein, "invert emulsion" or "oil-in-water emulsion" is understood to mean the liquid portion of the drilling fluid comprising an emulsion (excluding solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

In the method of this invention, a composition or compound having the
20 following formula (I) is added to the invert emulsion or oil-based drilling fluid (or well service fluid) to reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity at low temperatures. The compound may be added to the fluid during initial preparation of the fluid or later as the fluid is being used for drilling or well
25 service purposes in the formation. The quantity added is an effective amount to maintain or effect the desired viscosity of the drilling fluid. For purposes of this invention, an "effective amount" of thinner of formula (I) is preferably from about 0.5 to about 15 pounds per barrel of drilling fluid or mud. A more preferred amount of thinner ranges from about 1 to about 5 pounds per barrel
30 of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid.

Formula (I) is:



where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. Preferably, R has about 8 to about 18 carbon atoms; more preferably, R has about 12 to about 18 carbon atoms; and most preferably, R has about 12 to about 14 carbon atoms. Also, most preferably, R is saturated and linear.

The compositions or compounds of formula (I) may be prepared by customary techniques of alkoxylation, such as alkoxyating the corresponding fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides. Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (I), the subscripts n and m respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one molecule of the alkoxyated fatty alcohol. The subscript k indicates the number of butylene oxide (BO) molecules or groups. The subscripts n, m, and k need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (I) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow, such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (I) must contain at least one ethoxy group. Preferably, the compound of formula I will also contain at least one propoxy group (C_3H_7O-) or butoxy group (C_4H_9O-). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (I) will have a value for m ranging from about 1 to about 10 with k zero or a value for k ranging from about 1 to about 10 with m zero. Most preferably, m will be about 1 to about 10 and k will be zero.

5 Other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (I) above will have n ranging from about 2 to about 5, and m being about 3 or about 4 with k zero. It is particularly advantageous to
10 establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (I) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

Additional preferred compounds for use in the invention having formula (I) above will have alkyl radicals containing about 12 to about 18 carbon atoms,
15 or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

Used as thinners according to the method of the invention, the compounds of formula (I) reduce the viscosity or lower the yield point of the drilling fluid to which they are added. These thinners are particularly effective
20 at low temperatures, i.e., temperatures at or below about 50°F (about 10°C) and most particularly effective at temperatures at or below about 40°F (about 4°C). The lower limit of effectiveness for these thinners is about 14°F (about -10°C). The thinners do not significantly influence or affect the rheology of drilling fluids at high temperatures, particularly temperatures ranging from about
25 100 to about 250° F or more.

The compounds of formula (I) are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

Example drilling fluids comprising invert (water-in-oil) emulsions of
30 particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and

polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at temperatures above about 32°F (about 0°C) or at least as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

10

- (a) most preferably, carboxylic esters of the formula:



15

where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 5 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 22 carbon atoms;

20

- (b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;
- (c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;
- (d) water-insoluble alcohols of the formula:



25

where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

- (e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis; European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic

diesters). Carboxylic esters of formula (II) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

- 5 In a preferred embodiment of this invention, compounds of formula (I) are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (II) where the radical R' in formula (II) is an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms).
- 10 Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.
- 15 For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters
- 20 disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.

The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50 % by volume of one or more
25 preferred compounds (a) - (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.

Water is preferably present in the liquid phase of the drilling fluids used
30 in the invention, and preferably in amounts not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, thinners of formula (I) are added to drilling fluids comprising invert emulsions containing about 15 to about 35% by volume water and more

preferably 20% by volume water and about 80% by volume oil phase. To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts and/or sodium salts. CaCl_2 in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following rheology: plastic viscosity (PV) in the range of about 10 to about 60 cP, and preferably in the range of about 15 to about 40 cP, and yield point (YP) in the range of about 5 to about 40 lb/100 ft², and preferably in the range of about 10 to about 25 lb/100 ft², at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F (about 4°C), the YP should not exceed about 75 lb/100 ft², and should preferably be in the range of about 10 to about 65 lb/100 ft², more preferably about 15 to about 45 lb/100 ft², and most preferably less than about 35 lb/100 ft². A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft².

Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA), incorporated herein by reference.

The solids content (not including low gravity solids), or the amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids, or weighting agents, which serve to increase the density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly.

Drilling fluids used in this invention may optionally also contain other additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO₂ and H₂S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids range from
5 about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an alternative to lime may also be used to adjust and/or stabilize Invert emulsions of the
10 drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added.
15 Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

Although the invention has primarily been described in the context of a
20 method of using compounds of formula (I) as thinners for drilling fluids at low temperatures, the compounds of formula (I) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids at low temperatures.

Further description and use of the invention is shown by the following
25 examples:

Examples

To show the effect of the invention, the following experiments were
30 conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

Ester	bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
CaCl ₂ x 2 H ₂ O	lb	27.2
Barite	lb	314.0
Dispersing auxiliary	lb	0.5

Thinner	lb/bbl	2.0
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The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid
 5 Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and with a C_{12/14} fatty alcohol sulfate + 2 EO, sodium salt (C2), with a C₁₂ ether sulfate, sodium salt (C3) and with an oleic acid sulfonate disodium salt (C4), respectively, as prior art thinners, and comparison was made with these
 10 thinners and with compounds of formula (I) in accordance with the invention. The formula (I) compounds used for this purpose were as follows:

- | | | |
|----|----|--|
| | E1 | C12/C14 fatty alcohol containing 2 EO and 4 PO |
| | E2 | C12/C14 fatty alcohol containing 5 EO and 4 PO |
| 15 | E3 | C12/C18 fatty alcohol containing 5 EO and 4 PO |
| | E4 | C12/C14 fatty alcohol containing 6 EO and 4 PO |

The invert muds were prepared in a conventional manner and subsequently, at 40°F and 122°F, the rheological characteristics of plastic
 20 viscosity (PV) and yield point (YP) and the gel strength after 10 seconds and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.

Measurements E5, E6 and E7 were carried out using the thinners E1, E2 and E4, but in contrast to the details above, 45 lb of solids (rev dust, i.e., filter ash) were also added to each of the muds, in order to demonstrate the advantageous action of the compounds of formula (I) used in accordance with the invention in the case of high solids loading of the emulsions. In these cases, the measurements were taken only after 16 hours of aging at 150°F. The thinner was not added to the muds E5 to E7 until after aging.

The results of the measurements are given in Tables 1a and 1b below.

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Table 1a

	C1	C1	C2	C2	C3	C3	C4	C4	E1	E1	E2	E2	E3	E3	E4	E4
Temp. °F	40	122	40	122	40	122	40	122	40	122	40	122	40	122	40	122
PV (cP)	84	28	105	30	n.m.	33	91	24	83	31	87	28	94	28	83	29
YP lb/100 ft ²	68	28	71	35	n.m.	62	69	20	70	41	34	33	62	41	30	30
Gels 10"/10'	27/29	12/13	24/29	15/15	n.m.	28/31	25/25	9/7	25/28	17/19	11/13	14/16	20/24	17/18	8/11	13/14

n.m.: not measurable

Table 1b - Measurements with addition of 45 lb rev dust

	C1	C1	E5	E5	E6	E6	E7	E7
Temperature °F	40	122	40	122	40	122	40	122
PV (cP)	84	28	107	37	108	40	108	37
YP lb/100 ft ²	68	28	37	23	72	42	48	30
Gels 10"/10'	27/29	12/13	12/14	7/9	25/30	14/18	17/18	12/14

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the compounds of formula (I) used in the method and in the emulsions of the invention, especially at low temperatures, in comparison to the prior art. The higher plastic viscosity for E5 to E7 is attributable
5 to the higher proportion of solids in the mud systems.

Further experiments may be seen in Tables 2 to 9. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. This illustrates particularly well the advantageous influence of the compounds of formula (I) on the rheology at low temperatures (40°F, 4°C)
10 without any marked influence at high temperatures (120°F, 50°C). The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

15 In Tables 2 to 9:

PETROFREE LV® is 2-ethylhexyl octanoate (from Cognis, Germany)

PETROFREE LE® is linear alpha-olefin (from Cognis, Germany)

PETROFREE® is C8-14 fatty acid 2-ethylhexyl ester (from Cognis, Germany)

20 GELTONE II® is organophilic bentonite (from Baroid, Houston, Texas)

Thinner E1 is Formula I C12/C14 fatty alcohol of the invention containing 2 EO and 4 PO

Thinner E2 is Formula I C12/C14 fatty alcohol of the invention containing 5 EO and 4PO

25

Table 2

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids					
E2, lb/bbl	0	3	5			
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	113	34	107	35
Yield point, lb/100ft ²	38	14	25	14	19	13
10 sec gel, lb/100ft ²	16	8	10	8	6	8
10 min gel, lb/100ft ²	22	11	13	8	9	8
Fann 35 dial readings						
600 rpm	274	94	251	82	233	83
300 rpm	156	54	138	48	126	48
200 rpm	114	40	97	35	88	35
100 rpm	70	25	56	22	49	22
6 rpm	17	6	10	7	7	6
3 rpm	14	5	7	6	5	5

Table 3

5

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	128	50
Yield point, lb/100ft ²	230	152	19	125
10 sec gel, lb/100ft ²	108	64	10	50
10 min gel, lb/100ft ²	110	68	13	52
Fann 35 dial readings				
600 rpm	590	254	271	225
300 rpm	410	203	145	175
200 rpm	336	179	103	149
100 rpm	248	148	59	119
6 rpm	112	79	10	62
3 rpm	100	70	8	58

Table 4

Mud system	PETROFREE LV			
Mud weight, lb/gal	16.0			
Oil/water ratio	80/20			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	152	51	142	40
Yield point, lb/100ft ²	62	27	40	19
10 sec gel, lb/100ft ²	22	10	18	10
10 min gel, lb/100ft ²	48	26	22	12
Fann 35 dial readings				
600 rpm	366	129	324	99
300 rpm	214	78	182	59
200 rpm	158	59	130	45
100 rpm	98	38	78	30
6 rpm	24	11	16	10
3 rpm	20	9	12	9

Table 5

5

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	88	29
Yield point, lb/100ft ²	54	53	37	53
10 sec gel, lb/100ft ²	33	23	13	26
10 min gel, lb/100ft ²	38	27	17	30
Fann 35 dial readings				
600 rpm	318	115	213	111
300 rpm	188	84	125	82
200 rpm	139	71	90	70
100 rpm	91	54	56	55
6 rpm	35	25	15	28
3 rpm	32	21	13	25

Table 6

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	113	34
Yield point, lb/100ft ²	90	47	73	44
10 sec gel, lb/100ft ²	38	21	27	20
10 min gel, lb/100ft ²	44	24	30	22
Fann 35 dial readings				
600 rpm	310	115	299	112
300 rpm	200	81	188	78
200 rpm	157	67	142	64
100 rpm	110	50	95	48
6 rpm	42	23	31	22
3 rpm	38	21	27	19

5

Table 7

Mud system	PETROFREE LE			
Mud weight, lb/gal	16.4			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	173	40	107	43
Yield point, lb/100ft ²	21	9	18	7
10 sec gel, lb/100ft ²	16	8	11	8
10 min gel, lb/100ft ²	19	11	15	11
Fann 35 dial readings				
600 rpm	387	89	232	93
300 rpm	194	49	125	50
200 rpm	135	35	88	37
100 rpm	74	22	50	22
6 rpm	12	5	9	6
3 rpm	10	4	7	5

Table 8

Mud system	PETROFREE LE			
Mud weight, lb/gal	11.6			
E2, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	80	31	56	32
Yield point, lb/100ft ²	25	18	27	16
10 sec gel, lb/100ft ²	12	8	17	9
10 min gel, lb/100ft ²	20	11	23	11
Fann 35 dial readings				
600 rpm	185	80	139	80
300 rpm	105	49	83	48
200 rpm	77	37	63	37
100 rpm	46	24	43	24
6 rpm	11	7	14	8
3 rpm	9	6	13	7

Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	113	35
Yield point, lb/100ft ²	38	14	41	16
10 sec gel, lb/100ft ²	16	6	16	9
10 min gel, lb/100ft ²	22	11	20	11
Fann 35 dial readings				
600 rpm	274	94	267	86
300 rpm	156	54	154	51
200 rpm	114	40	114	39
100 rpm	70	25	71	26
6 rpm	17	6	18	8
3 rpm	14	5	14	8

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The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described composition and method can be made without departing from the intended scope of this invention as defined by the appended claims.

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We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid
comprising an invert emulsion, said method comprising adding to said
drilling fluid or well service fluid a compound having the formula:

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where R is a saturated or unsaturated, linear or branched alkyl radical
having about 8 to about 24 carbon atoms, n is a number ranging from about
1 to about 10, m is a number ranging from about 0 to about 10, and k is a
number ranging from about 0 to about 10.

15

2. The method of claim 1 wherein in said formula, k is zero and m is a number
ranging from about 1 to about 10, or m is zero and k is a number ranging
from about 1 to about 10.

20

3. The method of claim 1 wherein in said formula, n is a number ranging from
about 1 to about 6, m is a number ranging from about 1 to about 6, and k is
zero.

25

4. The method of claim 1 wherein said invert emulsion comprises a continuous
oil phase comprising compounds or compositions flowable and pumpable at
temperatures at least as low as about 40 degrees Fahrenheit.

30

5. The method of claim 1 wherein said invert emulsion comprises a continuous
oil phase comprising compounds or compositions flowable and pumpable at
temperatures above about 32 degrees Fahrenheit.
6. The method of claim 5 wherein said oil phase comprises compounds or
compositions selected from the group comprising:

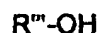
- (f) carboxylic esters of the formula:



where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

- (g) linear or branched olefins having about 8 to about 30 carbon atoms;
(h) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (i) water-insoluble alcohols of the formula:



where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

- (j) carbonic diesters.

7. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said drilling fluid or well service fluid.

8. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said drilling fluid or well service fluid at temperatures less than about 50 degrees Fahrenheit.

9. The method of claim 1 wherein said compound is added to said drilling fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said drilling fluid or well service fluid.

10. The method of claim 1 wherein said compound reduces the viscosity of said

drilling fluid or well service fluid at low temperatures.

11. The method of claim 10 wherein said compound does not significantly affect the viscosity of said fluid at high temperatures.

5

12. The method of claim 1 wherein said compound is added to said fluid when said fluid is prepared.

10

13. The method of claim 1 wherein said compound is added to said fluid while said fluid is circulating in a wellbore.

15

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and a compound having the formula:



20

where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

25

15. The drilling fluid or well service fluid of claim 14 wherein said compound is added in sufficient amounts to reduce the viscosity of said fluid at low temperatures.

30

16. The drilling fluid or well service fluid of claim 14 having a density of from about 8 to about 18 lbs/gal.

17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft² at about 40°F.

5 18. A method of reducing the viscosity of an invert emulsion drilling fluid or well service fluid at low temperatures comprising adding to said fluid an effective amount of compound having the formula:



10 where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

15 19. The method of claim 18 wherein said compound does not significantly affect the viscosity of the drilling fluid at high temperatures.

20. The method of claim 18 further comprising circulating said fluid in a wellbore and adding said compound to said fluid during said circulation.

20

21. The method of claim 18 further comprising preparing said fluid and adding said compound to said fluid during said preparation.

25

Abstract

A method of reducing the viscosity of oil-based drilling fluids and well service fluids at low temperatures and a thinner compound for use in such drilling fluids and well service fluids is disclosed. The method comprises adding to said
 5 drilling fluids or well service fluids a thinner having the formula:



where R is a saturated or unsaturated, linear or branched alkyl radical having
 10 about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

15

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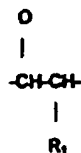
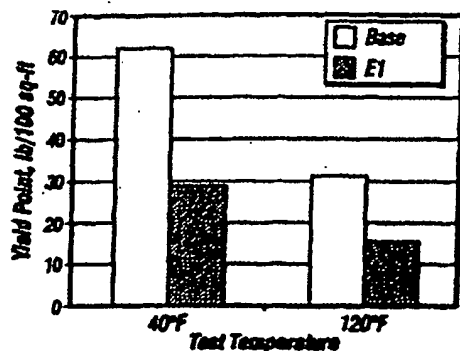
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(54) Title: THINNERS FOR INVERT EMULSIONS



(I)



(II)

carbon atoms.

(57) Abstract: A method of reducing the viscosity of invert emulsions and oil-based drilling fluids and well service fluids comprising such emulsions over a broad temperature range is disclosed. The method comprises adding to said invert emulsions of the invention a non-ionic surfactant alone or in combination with a co-thinner having the formula: $R^{**}-(C_2H_4O)_n(C_2H_4O)_m(C_2H_4O)_k-H$ where R^{**} is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. The non-ionic surfactant is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C_{10-22} carboxylic acids or C_{10-22} carboxylic acid derivatives containing at least in position 9/10 and/or 13/14 structural units of general formula (I) where R_1 is a hydrogen atom or an OH group or a group OR_2 . R_2 is an alkyl group of about 1 to about 18 carbon atoms, an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II); R_3 is a hydrogen atom, an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of 2 to 21

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REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

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This person is:

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THINNERS FOR INVERT EMULSIONS

Background of the Invention

1. Field of the Invention

5 This invention is generally related to methods and compositions for drilling and servicing wellbores in hydrocarbon bearing subterranean formations. Particularly, this invention is related to oil-based drilling fluid systems comprising water-in-oil invert emulsions, and to thinners that enhance or enable use of such fluids over a broad temperature range.

10 2. Description of Relevant Art

 A drilling fluid, or "mud" which a drilling fluid is also often called, is a specially designed fluid that is circulated in a wellbore as the wellbore is being drilled to facilitate the drilling operation. The various functions of a drilling fluid include removing drill cuttings from the wellbore, cooling and lubricating the drill
15 bit, aiding in support of the drill pipe and drill bit, and providing a hydrostatic head to maintain the integrity of the wellbore walls and prevent well blowouts. Specific drilling fluid systems are selected to optimize a drilling operation in accordance with the characteristics of a particular geological formation.

 A drilling fluid typically comprises water and/or oil or synthetic oil or other
20 synthetic material or synthetic fluid ("synthetic") as a base fluid, with solids in suspension. A non-aqueous based drilling fluid typically contains oil or synthetic as a continuous phase and may also contain water dispersed in the continuous phase by emulsification so that there is no distinct layer of water in the fluid. Such dispersed water in oil is generally referred to as an invert
25 emulsion or water-in-oil emulsion.

 A number of additives may be included in such oil based drilling fluids and invert emulsions to enhance certain properties of the fluid. Such additives may include, for example, emulsifiers, weighting agents, fluid-loss additives or fluid-loss control agents, viscosifiers or viscosity control agents, and alkali.
30 Further general discussion and description of oil-based drilling fluids is provided in P.A. Boyd, et al., New Base Oil Used In Low Toxicity Oil Muds, Journal of

Petroleum Technology, pages 137-142 (1985), which is incorporated herein by reference.

An essential criterion for assessing the utility of a fluid as a drilling fluid or as a well service fluid is the fluid's rheological parameters, particularly under drilling and wellbore conditions. For use as a drilling fluid, or as a fluid for servicing a well, the fluid must be capable of maintaining certain viscosities suitable for drilling and circulation in the wellbore. Preferably, a drilling fluid will be sufficiently viscous to be capable of supporting and carrying to the surface of the well drill cuttings without being so viscous as to interfere with the drilling operation. Moreover, a drilling fluid must be sufficiently viscous to be able to suspend barite and other weighting agents. However, increased viscosity can result in problematic sticking of the drill string, and increased circulating pressures can contribute to lost circulation problems.

Thinner may be added to the drilling fluid or drilling mud systems before and in the course of drilling. Anionic surfactants particularly from the group of the fatty alcohol sulfates, the fatty alcohol ether sulfates and the alkylbenzenesulfonates are examples of such thinners known in the prior art. Although such compounds have been shown to effect thinning of drilling fluids, their effectiveness as thinners is not always uniform over the entire range of temperatures (typically as low as about 40°F (or lower) to as high as about 250°F (or higher)) at which drilling fluids are used.

Thinner and other additives to drilling fluids, as well as drilling fluids employed in onshore and offshore wells, must commonly meet stringent environmental regulations related to biodegradability and toxicity. Further, drilling fluids and additives to drilling fluids must be able to withstand subterranean conditions that the fluids will typically encounter in a wellbore, such as high temperatures, high pressures, and pH changes.

A need exists for improved rheology-modifying or viscosity reducing additives to oil-based drilling fluids, and particularly to drilling fluids comprising invert (water-in-oil) emulsions, which are capable of being used over a broad range of temperatures. As used herein, unless indicated otherwise, a "broad

temperature range" shall be understood to generally mean temperatures ranging from about 14°F to about 350°F and preferably ranging from about 40°F to about 250°F.

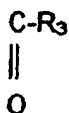
5 Summary of the Invention

According to the method of the present invention, at least one compound or composition is added to a water-in-oil or invert emulsion, or a drilling fluid or well service fluid comprising such emulsion, which reduces the viscosity of the emulsion over a broad temperature range or which enables or enhances the ability of the emulsion to maintain its viscosity over a broad temperature range. The compound or composition, which may be generally called a "thinner," continues to have this effect in a drilling fluid or well service fluid comprising the emulsion for use in drilling or servicing wellbores in subterranean formations, particularly hydrocarbon bearing subterranean formations, over a broad temperature range.

The first such thinner compound of the present invention is a non-ionic surfactant which is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9/10 and/or 13/14 having units of the general formula:



where R₁ is a hydrogen atom or an OH group or a group OR₂, where R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms or a group of the formula:



- 5 where R_3 is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of about 2 to about 21 carbon atoms.

This first thinner compound may be used alone or may be used in combination with a second or other thinner or "co-thinner" compound having the following formula:

10



- where R is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

The invention also comprises an invert emulsion drilling fluid or well service fluid containing this first thinner compound, or containing said first thinner compound in combination with said second thinner compound.

20

Brief Description of the Drawings

Figure 1 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 2.

- Figure 2 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 3.

Figure 3 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 4.

Figure 4 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 5.

- Figure 5 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 6.

Figure 6 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 7.

Figure 7 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 8.

5 Figure 8 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 9.

Figure 9 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 10.

10 Figure 10 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 11.

Figure 11 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 12.

Figure 12 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 13.

15 Figure 13 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 14.

Figure 14 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 15.

20 Figure 15 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 16.

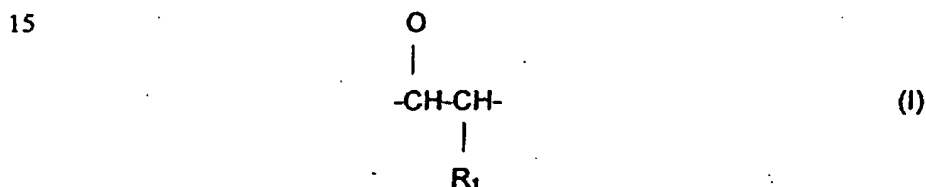
Figure 16 is a graph comparing yield point of mud systems with and without thinners of the invention tested as reported in Table 17.

Detailed Description of Preferred Embodiments

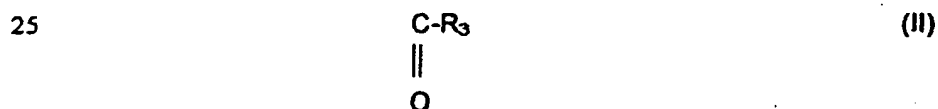
25 The present invention provides a method of influencing the rheology, and particularly reducing the viscosity, of invert (water-in-oil) emulsions and drilling fluids or well service fluids comprising such invert (water-in-oil) emulsions. The method is particularly applicable to fluids for use in wellbores penetrating hydrocarbon bearing subterranean formations. Such drilling fluids and well service fluids typically comprise a continuous oil phase, water
30 dispersed in the oil phase, solids insoluble in the drilling fluid or well service fluid suspended in the fluid, and various additives. As the term is used herein,

an "invert emulsion" or an "oil-in-water emulsion" is understood to mean the liquid portion of a drilling fluid comprising an emulsion (excluding any solids). The term "invert emulsion drilling fluid" means the total sum of what is circulated as a drilling fluid.

- 5 In the method of this invention, certain non-ionic surfactants are added to the invert emulsion or oil based drilling fluid (or well service fluid) to "thin" or reduce the viscosity of the fluid or to enhance the ability of the fluid to maintain its viscosity or to resist increasing viscosity over a broad range of temperatures. The particular non-ionic surfactants are reaction products of ethylene oxide, propylene oxide and/or butylene oxide with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 (and preferably one or two double bonds in position 9/10 and/or 13/14) having structural units of the general formula (I)



- 20 where R₁ is a hydrogen atom, or an OH group, or a group OR₂. R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II)



- 30 R₃ is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

The alkoxylation products may be prepared in accordance with the teaching of DE 39 23 394, which is incorporated herein by reference, by reacting the OH-containing carboxylic acid derivatives, for example, with

ethylene oxide, propylene oxide and/or butylene oxide in the presence of an appropriate catalyst at temperatures between about 110 and about 200°C and pressures between about 10^5 Pa and about 2×10^6 Pa.

- Suitable starting materials for OH-containing C_{10-22} carboxylic acids or
- 5 C_{10-22} carboxylic acid derivatives are unsaturated, naturally occurring and/or synthesizable C_{10-22} carboxylic acids or derivatives thereof containing carboxylic acid radicals having at least one or two double bonds in position 9, 10, 13 and/or 14. Examples of such unsaturated carboxylic acid derivatives are 9-dodecenoic acid, 9-tetradecenoic acid, 9-hexadecenoic acid, 9-octadecenoic
- 10 acid, 9-octadecenoic acid, 9,12-octadecadienoic acid, 9,12,15-octadecatrienoic acid, 9-icosenoic acid, 13-docosenoic acid, and mixtures containing a large amount (i.e., preferably at least about 60%) of such unsaturated carboxylic acids. As starting materials it is preferable to use carboxylic acids having about 16 to about 22 carbon atoms and at least one or two double bonds in position 9
- 15 and/or 13 or carboxylic acid mixtures containing at least a large amount (i.e., preferably at least about 80%) of carboxylic acids having about 16 to about 22 carbon atoms and at least one or two double bonds in position 9 and/or 13.

- Further examples of suitable unsaturated carboxylic acid derivatives for use in preparing thinner compounds for use in the invention are unsaturated
- 20 C_{10-22} carboxylic esters, such as for example, unsaturated C_{10-22} carboxylic acid alkyl esters with monohydric alcohols having about 1 to about 18 carbon atoms. Particularly appropriate are C_{10-22} carboxylic mono-, di- and/or triglycerides containing unsaturated C_{10-22} carboxylic acid radicals having at least one or two double bonds in position 9 and/or 13. Also suitable are esters of C_{10-22}
- 25 carboxylic acids with other polyols, such as for example ethylene glycol or trimethylolpropane.

- Unsaturated C_{10-22} carboxylic acid C_{1-18} alkyl esters are obtainable by esterifying the corresponding unsaturated carboxylic acid or by transesterifying the corresponding mono-, di- and/or triglycerides with C_{1-18} alkyl alcohols, such
- 30 as, for example, methanol, ethanol, propanol, butanol, isobutanol, 2-ethylhexanol, decanol and/or stearyl alcohol. Examples of such unsaturated

C₁₀₋₂₂ carboxylic acid C₁₋₁₈ alkyl esters are methyl palmitate, methyl oleate, ethyl oleate, isobutyl oleate, 2-ethylhexyl oleate and/or dodecyl oleate and/or C₁₀₋₂₂ carboxylic acid C₁₋₁₈ alkyl ester mixtures containing at least a large fraction (i.e., at least about 60%) of those C₁₀₋₂₂ carboxylic acid C₁₋₁₈ alkyl esters whose carboxylic acid radicals have at least one or two double bonds in position 9 and/or 13, such as, for example, palm oil methyl ester, soya oil methyl ester, colza oil methyl ester and/or tallow fatty acid ethyl ester. Other suitable starting materials for preparing the alkoxylation products for use in the invention are fats and oils of natural origin whose carboxylic acid content is comprised predominantly of unsaturated C₁₀₋₂₂ carboxylic acids having at least one or two double bonds in position 9 and/or 13, such as, for example, olive oil, linseed oil, sunflower oil, soya oil, groundnut oil, cottonseed oil, colza oil, palm oil, lard and tallow.

Unsaturated C₁₀₋₂₂ carboxylic acids and/or C₁₀₋₂₂ carboxylic acid derivatives may be epoxidized to the OH-containing compounds, for example, by reaction with peracetic acid in the presence of acidic catalysts or with performic acid formed *in situ* from formic acid and hydrogen peroxide. The oxirane rings of the epoxidized carboxylic acids and/or carboxylic acid derivatives are subsequently cleaved open to form hydroxyl groups by reaction with hydrogen or protic compounds, such as water, straight-chain and/or branched-chain alkyl and /or alkenyl alcohols having about 1 to about 18 carbon atoms or straight-chain and/or branched-chain, saturated and/or unsaturated C₁₋₁₈ carboxylic acids. Other natural or synthetic compounds comprising epoxide-containing carboxylic acids or carboxylic acid derivatives, such as castor oil or hydrogenated castor oil, may also be used. The cleavage conditions are chosen such that the acid-derivative groups and acid groups present remain intact.

The reaction of epoxidized carboxylic acid derivatives and/or epoxidized carboxylic acids with protic compounds may be carried out, for example, in accordance with the processes described in DE 39 23 394.

The carboxylic acids and/or carboxylic acid derivatives obtained by cleaving the oxirane rings, containing carboxylic acid radicals having at least one OH group in position 9, 10, 13 and/or 14, are subsequently reacted by known industrial processes with ethylene oxide, propylene oxide and/or butylene oxide (preferably with ethylene oxide and/or propylene oxide).

Alkoxylation products obtained by alkoxyating compounds of the formula (I) in which R_1 is a group OR_2 and R_2 is a radical of the formula (II) are preferred. Compounds where the radical R_3 is an alkyl group of about 8 to about 16 carbon atoms, most preferably about 8 to about 10 carbon atoms, are also preferred.

Some non-ionic surfactant compounds that could possibly be used as thinners in accordance with the present invention are also described in WO98/19043 of Henkel Kommandiegesellschaft auf Aktien. That international application teaches use of the compounds in the oil and gas industry as cleaning agents, in contrast to the use of the present invention.

Used as thinners according to the method of the invention, the non-ionic surfactants of the present invention reduce the viscosity or lower the yield point of the drilling fluid to which they are added over a broad range of temperatures.

Example drilling fluids comprising invert (water-in-oil) emulsions of particular use in the method of the invention generally have an oil phase comprising diesel oil, paraffin oil and/or mineral oil, or a synthetic oil. Alternatively, other carrier fluids may be used such as carboxylic esters, alcohols, ethers, internal olefins, alphaolefins (IO and/or AO), and polyalphaolefins (PAO), which may be branched or unbranched but are preferably linear and preferably ecologically acceptable (non-polluting oils). Preferably, the oils or carrier fluids used for the oil phase of the drilling fluid will be comprised of compounds which are flowable and pumpable at temperatures above about 32°F (about 0°C) or as low as about 40°F (about 5°C) as well as at higher temperatures. For example, compounds selected from one or more of the following groups or classes below are believed particularly suitable to comprise the oil phase of drilling fluids used in the present invention:

- (a) most preferably, carboxylic esters of the formula:



5 where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

- (b) also preferably, linear or branched olefins having about 8 to about 30 carbon atoms;

10 (c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

- (d) water-insoluble alcohols of the formula:



15 where R''' is a saturated, unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms; and

- (e) carbonic diesters.

Such suitable oils are taught further, for example, in: European Patent
20 Applications 0 374 671, 0 374,672, 0 382 070, and 0 386 638 of Cognis; European Laid-Open Specification 0 765 368 of Cognis (linear olefins); European Application 0 472 557 (water insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin containing about 1 to about 24 carbon atoms); European Application 0 532 570 (carbonic
25 diesters). Carboxylic esters of formula (III) above are preferred for the oil phase of drilling fluids used in this invention and particularly preferred are the esters described in European Laid-Open Specification EP 0 374 672 and EP 0 386 636.

30 In a preferred embodiment of this invention, non-ionic surfactants of the invention are added to drilling fluids comprising invert emulsions having an oil phase comprising esters of formula (III) where the radical R' in formula (III) is

an alkyl radical having about 5 to about 21 carbon atoms (or more preferably about 5 to about 17 carbon atoms or most preferably about 11 to about 17 carbon atoms). Particularly suitable alcohols for making such esters are branched or unbranched alcohols with about 1 to about 8 carbon atoms, for example, methanol, isopropanol, isobutanol, and 2-ethylhexanol. Alcohols having about 12 to about 18 carbon atoms may alternatively be preferred for making other esters suitable for the invention.

For example, additional preferred esters for the oil phase of drilling fluids used in the invention include, without limitation: saturated C12-C14 fatty acid esters and unsaturated C16-C18 fatty acids (with isopropyl-, isobutyl- or 2-ethylhexanol as the alcohol component); 2-ethylhexyl octanoate; acetic acid esters, especially acetates of C8-C18 fatty alcohols; branched carboxylic esters disclosed in WO 99/33932 of Chevron or EP 0 642 561 of Exxon; alpha olefin mixtures disclosed in EP 0 765 368 A1 of Cognis and Halliburton; and blends of these various esters.

The oil phase of the emulsions of the drilling fluids used in the invention is preferably comprised of at least about 50% by volume of one or more preferred compounds (a) - (e) above. More preferably, such preferred compounds comprise about 60% to about 80% by volume of said oil phase, and most preferably, such preferred compounds comprise about 100% of the oil phase.

Water is preferably present in the liquid phase of the emulsions of the drilling fluids used in the invention in amounts preferably not less than about 0.5% by volume (excluding solids in the liquid phase). In a preferred embodiment of this invention, the nonionic surfactant thinners of the present invention are added to drilling fluids (preferably comprising invert emulsions) containing about 15% to about 35% by volume water and more preferably about 20% by volume water and about 80% by volume oil phase.

To compensate for the osmotic gradient between the drilling mud and the formation or connate water, water in drilling fluids used in the present invention typically includes fractions of electrolytes, such as calcium salts

and/or sodium salts. CaCl_2 in particular is frequently used, although other salts from the group of alkali metals and/or alkaline earth metals are also suitable, with potassium acetates and formates being common examples.

Preferred drilling fluids used in this invention have the following rheology: plastic viscosity (PV) preferably in the range of about 10 to about 60 cP, and more preferably in the range of about 15 to about 40 cP, and yield point (YP) preferably in the range of about 5 to about 40 lb/100 ft², and more preferably in the range of about 10 to about 25 lb/100 ft², when measured at about 122°F (about 50°C). At lower temperatures, i.e., at or below about 40°F (about 4°C), the YP should not exceed about 75 lb/100 ft², and should preferably be in the range of about 10 to about 65 lb/100 ft², more preferably about 15 to about 45 lb/100 ft², and most preferably less than about 35 lb/100 ft². A preferred practicable lower limit for YP for drilling fluids used in this invention is about 5 lb/100 ft².

Methods for determining these parameters of PV and YP are well known to those skilled in the art. An example reference is "Manual of Drilling Fluids Technology", particularly the chapter on Mud Testing, available from Baroid Drilling Fluids, Inc., in Houston, Texas (USA) and Aberdeen, Scotland, incorporated herein by reference.

The solids content (not including low gravity solids), or amount of weighting agents, in drilling fluids used in this invention is preferably about 0 to about 500 lb/bbl, and most preferably about 150 to about 350 lb/bbl. The mud weight, i.e., the density of the drilling fluids, is preferably in the range of about 8 to about 18 lb/gal. and more preferably about 9 to about 15 lb/gal. Such solids, or weighting agents, which serve to increase density of the drilling fluids, may be any solids known to those skilled in the art as useful for such purpose, but will preferably be inert or environmentally friendly. Barite and barium sulfate are examples of commonly used weighting agents.

Drilling fluids used in this invention may optionally also contain other additives known to those skilled in the art, such as fluid-loss control additives and emulsifiers. Alkali may also be used, preferably lime (calcium hydroxide

or calcium oxide), to bind or react with acidic gases (such as CO₂ and H₂S) encountered during drilling in the formation. Such alkali, or an alkali reserve, is known to prevent hydrolysis by acidic gases of generally acid-labile esters of the drilling fluid. Preferred quantities of free lime in the drilling fluids may range
 5 from about 1 to about 10 lbs/bbl, and more preferably about 1 to about 4 lbs/bbl, although lower ranges such as less than about 2 lbs/bbl are preferred for certain esters that tend to hydrolyze in the presence of alkaline compounds as will be known to those skilled in the art. Other suitable agents as an
 10 alternative to lime may also be used to adjust and/or stabilize invert emulsions of the drilling fluids with respect to acids. An example of such alternative agents is a protonated amine, as described in U.S. Patent No. 5,977,031.

Further optional additives that may be present in the drilling fluids used in this invention include electrolytes, such as calcium chloride, organophilic bentonite and organophilic lignite. Glycols and/or glycerol may also be added.
 15 Still further, dispersion aids, corrosion inhibitors and/or defoamers may be used. These and other suitable auxiliaries and additives are used in amounts known to those skilled in the art depending on the conditions of the particular wellbore and subterranean formation.

In an alternative embodiment of the present invention, in addition to the
 20 non-ionic surfactant thinners of the present invention described above, additional thinners may be added advantageously in combination with said non-ionic surfactant thinners. Such particularly advantageous co-thinners are alkoxyated compounds of the general formula (V) :



where R'' is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging
 30 from about 0 to about 10. Preferably, R'' has about 8 to about 18 carbon atoms; more preferably, R'' has about 12 to about 18 carbon atoms; and most

preferably, R''' has about 12 to about 14 carbon atoms. Also, most preferably, R''' is saturated and linear.

The compositions or compounds of formula (V) may be prepared by customary techniques of alkoxylation, such as alkoxyating the corresponding fatty alcohols with ethylene oxide and/or propylene oxide or butylene oxide under pressure and in the presence of acidic or alkaline catalysts as is known in the art. Such alkoxylation may take place blockwise, i.e., the fatty alcohol may be reacted first with ethylene oxide, propylene oxide or butylene oxide and subsequently, if desired, with one or more of the other alkylene oxides. Alternatively, such alkoxylation may be conducted randomly, in which any desired mixture of ethylene oxide, propylene oxide and/or butylene oxide is reacted with the fatty alcohol.

In formula (V), the subscripts n and m respectively represent the number of ethylene oxide (EO) and propylene oxide (PO) molecules or groups in one molecule of the alkoxyated fatty alcohol. The subscript k indicates the number of butylene oxide (BO) molecules or groups. The subscripts n, m, and k need not be integers, since they indicate in each case statistical averages of the alkoxylation. Included without limitation are those compounds of the formula (V) whose ethoxy, propoxy, and/or butoxy group distribution is very narrow, such as for example, "narrow range ethoxylates" also called "NREs" by those skilled in the art.

To accomplish the purposes of this invention, the compound of formula (V) must contain at least one ethoxy group and may have up to or about 10 ethoxy groups. Preferably, the compound of formula (V) will also contain at least one propoxy group (C₃H₇O-) or butoxy group (C₄H₉O-). Mixed alkoxides containing all three alkoxide groups—ethylene oxide, propylene oxide, and butylene oxide—are possible for the invention but are not preferred.

Preferably, for use according to this invention, the compound of formula (V) will have a value for m ranging from about 1 to about 10 with k zero or a value for k ranging from about 1 to about 10 with m zero. Most preferably, m will be about 1 to about 10 and k will be zero.

Other preferred compounds for use in the invention having the formula (V) above will have n ranging from about 1 to about 6, m ranging from about 1 to about 6, and k zero. Still other preferred compounds for use in the invention having the formula (V) above will have n ranging from about 2 to about 5, and
5 m being about 3 or about 4 with k zero. It is particularly advantageous to establish the distribution of ethylene oxide and propylene oxide groups in the compounds of formula (V) in an ethylene oxide to propylene oxide ratio of about 1:1 to about 2:1, or even more preferably, about 2:1.5.

Additional preferred compounds for use in the invention having formula
10 (V) above will have alkyl radicals containing about 12 to about 18 carbon atoms, or more preferably about 12 to about 14 carbon atoms, with subscripts n and m each having values of about 4 or about 5.

Both the non-ionic surfactant thinners of the present invention and the thinners of formula (V) may be added to the drilling fluid (or well service fluid)
15 during initial preparation of the fluid or later as the fluid is being used for drilling or well service purposes in the formation. Alternatively, the non-ionic surfactant thinners may be added first at either of these times and the thinners of formula (V) may be added later. In still another embodiment, the thinners of formula (V) may be added first during either of these times and the non-ionic surfactant
20 thinners of the invention may be added later.

The quantity of thinners added is an effective amount to maintain or effect the desired viscosity of the drilling fluid, preferably or particularly over a broad temperature range. For purposes of this invention, an "effective amount" of non-ionic surfactant thinner is preferably from about 0.5 to about 15 pounds
25 per barrel of drilling fluid or mud. A more preferred amount of surfactant thinner ranges from about 1 to about 5 pounds per barrel of drilling fluid and a most preferred amount is about 1.5 to about 3 pounds thinner per barrel of drilling fluid. When the non-ionic surfactant thinners are used with formula (V) thinners, it is preferred to use the non-ionic surfactant thinners of the present
30 invention and the thinners of formula (V) in proportions of from about 1:1 to about 10:1.

The thinners of the present invention are biodegradable and are of little or no toxicity. They are expected to be capable of meeting increasingly stringent environmental regulations affecting the oil and gas industry worldwide.

Although the invention has primarily been described in the context of a method of using non-ionic surfactants alone and in combination with the compounds of formula (V) as thinners for drilling fluids over a broad temperature range, these non-ionic surfactants alone and in combination with compounds of formula (V) may also be effective as thinners for well service fluids such as spotting fluids or workover fluids over a broad temperature range.

Further description and use of the invention is shown by the following examples:

Examples

To show the effect of the invention, the following experiments were conducted. In each case an invert emulsion drilling mud system of the following general composition was prepared:

Ester	Bbl	0.496
Water	bbl	0.233
Emulsifier	lb	6.0
Organophilic bentonite	lb	1.0
Organophilic lignite	lb	5.0
Alkali reserve (lime)	lb	1.5
CaCl ₂ x 2 H ₂ O	lb	27.2
Barite	lb	314.0
Rev. dust	lb	45.5
Dispersing auxiliary	lb	0.5

Thinner	lb/bbl	3.0
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The oil phase (A) used was a 2-ethylhexyl octanoate as disclosed in EP 0 386 636. The emulsifier used was the product EZ MUL NTE (Baroid Drilling Fluids Inc., Houston, Texas). The oil/water ratio was 70/30 in each case. Measurements were carried out on a system without thinner (C1), and
5 with four non-ionic surfactant thinners E1 to E4 of the invention.

- E1 RS1100™, of Cognis, Germany, see below
- E2 like E1, but reacted with 39 parts of ethylene oxide
- E3 like E1, but reacted with no parts of ethylene oxide
- 10 E4 like E3, but reacted with 25 parts of ethylene oxide
- E5 like E1, but reacted with 50 parts of ethylene oxide

E1 was prepared according to the procedure described in U.S. Patent NO. 5,237,080 to Dante et al., assigned to Henkel Kommandiengesellschaft auf
15 Aktien, by reacting fatty acids (60% C₈, 35% C₁₀, AN = 361.9) with soya oil epoxide and distilling the product to obtain a clear yellow polyol (viscosity = 5550 mPas; 20°C; OHN = 105, SN = 236, AN = 3.1). This reaction product was then admixed with potassium hydroxide in methanol and heated, after which all traces of methanol were removed. The product was then reacted with
20 61 parts of ethylene oxide at a pressure not exceeding 5 bar to yield, after neutralization, a clear yellow liquid (OHN = 54.7). This product may be obtained from Cognis, Germany, under the tradename RS 1100.

The invert drilling fluids or muds were prepared in a conventional manner and subsequently, at 40°F and 120°F, the rheological characteristics of plastic viscosity (PV) and yield point (YP) and the gel strength after 10 seconds
25 and 10 minutes using a Fann SR12 rheometer (from Fann) were determined.

The results of the measurements are given in Table 1:

The data, especially for the yield point (YP), clearly indicate the advantageous thinning effect of the non-ionic surfactant thinners used according to the invention.

Further experiments may be seen in Tables 2 to 17. In these cases, the yield point (YP) of the systems tested was investigated at different temperatures and depicted as a graph. The measurements were carried out using a Fann 35 viscometer (from Fann). The tables also indicate the dial readings at different speeds of rotation per minute (rpm).

In Tables 2 to 17:

	PETROFREE LV ®	is 2-ethylhexyl octanoate (Cognis, Germany)
10	PETROFREE®	is C8-14 fatty acid 2-ethylhexyl ester (Cognis)
	GELTONE II®	is organophilic bentonite (Baroid, Houston, Texas)
	Thinner E1	is RS 1100™ (Cognis)

Table 2

Mud system	PETROFREE			
Mud weight, lb/gal	9.5			
Oil/water ratio	70/30			
E1, lb/bbl	0	1		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	75	26	78	23
Yield point, lb/100ft ²	62	31	29	15
10 sec gel, lb/100ft ²	26	16	23	8
10 min gel, lb/100ft ²	27	17	23	10
Fann 35 dial readings				
600 rpm	212	83	185	61
300 rpm	137	57	107	38
200 rpm	110	47	79	30
100 rpm	77	36	49	20
6 rpm	30	18	14	9
3 rpm	26	16	11	7

Table 3

5

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E1	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	140	36
Yield point, lb/100ft ²	230	152	19	8
10 sec gel, lb/100ft ²	108	64	7	3
10 min gel, lb/100ft ²	110	68	13	4
Fann 35 dial readings				
600 rpm	590	254	299	80
300 rpm	410	203	159	44
200 rpm	336	179	110	30
100 rpm	248	146	62	18
6 rpm	112	79	8	3
3 rpm	100	70	6	2

Table 4

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	11	34	108	35
Yield point, lb/100ft ²	90	47	27	7
10 sec gel, lb/100ft ²	38	21	4	3
10 min gel, lb/100ft ²	44	24	7	5
Fann 35 dial readings				
600 rpm	310	115	243	77
300 rpm	200	81	135	42
200 rpm	157	67	95	30
100 rpm	110	50	52	17
6 rpm	42	23	7	3
3 rpm	38	21	5	2

5 Table 5

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E1, lb/bbl	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	62	18
Yield point, lb/100ft ²	54	53	11	3
10 sec gel, lb/100ft ²	33	23	3	2
10 min gel, lb/100ft ²	38	27	5	3
Fann 35 dial readings				
600 rpm	318	115	135	39
300 rpm	188	84	73	21
200 rpm	139	71	52	14
100 rpm	91	54	29	9
6 rpm	35	25	4	2
3 rpm	32	21	3	1

Table 6

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E1, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	106	45
Yield point, lb/100ft ²	38	14	32	10
10 sec gel, lb/100ft ²	18	6	7	3
10 min gel, lb/100ft ²	22	11	8	5
Fann 35 dial readings				
600 rpm	274	94	244	100
300 rpm	156	54	138	55
200 rpm	114	40	98	39
100 rpm	70	25	55	22
6 rpm	17	6	8	4
3 rpm	14	5	5	3

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Table 7

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	37	100	31
Yield point, lb/100ft ²	53	20	15	4
10 sec gel, lb/100ft ²	20	8	6	3
10 min gel, lb/100ft ²	30	14	10	5
Fann 35 dial readings				
600 rpm	273	94	215	66
300 rpm	163	57	115	35
200 rpm	124	42	80	25
100 rpm	80	27	44	15
6 rpm	23	8	7	3
3 rpm	19	7	5	2

Table 8

Mud system	PETROFREE	
Mud weight, lb/gal	9.5	
Oil/water ratio	70/30	
E5, lb/bb	0	3
Temperature, °F	120	120
Plastic viscosity, cP	22	21
Yield point, lb/100ft ²	39	16
10 sec gel, lb/100ft ²	16	8
10 min gel, lb/100ft ²	17	10
Fann 35 dial readings		
600 rpm	83	58
300 rpm	61	37
200 rpm	52	28
100 rpm	40	20
6 rpm	19	8
3 rpm	17	7

5 Table 9

Mud system	PETROFREE LV			
Mud weight, lb/gal	9.5			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0	3		
Temperature, °F	40	120	40	120
Plastic viscosity, cP	65	20	52	20
Yield point, lb/100ft ²	31	33	27	17
10 sec gel, lb/100ft ²	29	17	17	10
10 min gel, lb/100ft ²	32	22	26	15
Fann 35 dial readings				
600 rpm	151	73	131	57
300 rpm	96	53	79	37
200 rpm	78	44	66	30
100 rpm	57	34	29	20
6 rpm	29	18	14	9
3 rpm	27	16	12	8

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Table 10

Mud system	PETROFREE			
Mud weight, lb/gal	14.0			
Oil/water ratio	75/25			
Contaminant	Excess GELTONE II			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	180	51	175	47
Yield point, lb/100ft ²	230	152	34	10
10 sec gel, lb/100ft ²	108	64	10	3
10 min gel, lb/100ft ²	110	66	14	5
Fann 35 dial readings				
600 rpm	590	254	384	104
300 rpm	410	203	209	57
200 rpm	336	179	148	40
100 rpm	248	146	82	23
6 rpm	112	79	12	3
3 rpm	100	70	9	2

5 Table 11

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Drill solids			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	110	34	106	30
Yield point, lb/100ft ²	90	47	20	9
10 sec gel, lb/100ft ²	38	21	8	5
10 min gel, lb/100ft ²	44	24	11	9
Fann 35 dial readings				
600 rpm	310	115	232	69
300 rpm	200	81	126	39
200 rpm	157	67	88	28
100 rpm	110	50	49	17
6 rpm	42	23	9	5
3 rpm	38	21	7	4

Table 12

Mud system	PETROFREE			
Mud weight, lb/gal	11.0			
Oil/water ratio	70/30			
Contaminant	Excess GELTONE II			
E5, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	132	31	90	23
Yield point, lb/100ft ²	54	53	20	9
10 sec gel, lb/100ft ²	33	23	6	2
10 min gel, lb/100ft ²	38	27	9	3
Fann 35 dial readings				
600 rpm	318	115	200	55
300 rpm	186	84	110	32
200 rpm	139	71	77	22
100 rpm	91	54	42	13
6 rpm	35	25	6	2
3 rpm	32	21	4	1

Table 13

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E1, lb/bbl	0		1	
E2, lb/bbl	0		2	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	105	33
Yield point, lb/100ft ²	38	14	15	6
10 sec gel, lb/100ft ²	16	6	7	3
10 min gel, lb/100ft ²	22	11	12	6
Fann 35 dial readings				
600 rpm	274	94	225	72
300 rpm	156	54	120	39
200 rpm	114	40	83	28
100 rpm	70	25	45	16
6 rpm	17	6	7	3
3 rpm	14	5	5	2

Table 14

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids (5%)					
E2, lb/bbl	0		3		5	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	118	40	111	35	114	37
Yield point, lb/100ft ²	38	14	26	7	17	2
10 sec gel, lb/100ft ²	16	6	13	5	6	2
10 min gel, lb/100ft ²	22	11	22	8	9	4
Fann 35 dial readings						
600 rpm	274	94	248	77	245	76
300 rpm	156	54	137	42	131	39
200 rpm	114	40	98	30	91	27
100 rpm	70	25	57	18	50	16
6 rpm	17	6	12	4	6	2
3 rpm	14	5	10	3	4	1

Table 15

Mud system	PETROFREE LV					
Mud weight, lb/gal	14.0					
Oil/water ratio	70/30					
Contaminant	Drill solids (10%)					
E2, lb/bbl	0		5		7	
Temperature, °F	40	120	40	120	40	120
Plastic viscosity, cP	176	59	152	48	150	47
Yield point, lb/100ft ²	48	19	14	6	20	4
10 sec gel, lb/100ft ²	16	9	8	6	8	3
10 min gel, lb/100ft ²	28	17	13	8	10	4
Fann 35 dial readings						
600 rpm	400	137	318	104	320	98
300 rpm	224	78	166	56	170	51
200 rpm	170	57	115	40	118	36
100 rpm	100	34	62	23	64	20
6 rpm	18	8	8	4	8	3
3 rpm	14	7	7	3	6	2

Table 16

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E3, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	115	36
Yield point, lb/100ft ²	38	14	35	14
10 sec gel, lb/100ft ²	16	6	25	6
10 min gel, lb/100ft ²	22	11	30	9
Fann 35 dial readings				
600 rpm	274	94	265	86
300 rpm	156	54	150	50
200 rpm	114	40	110	37
100 rpm	70	25	65	23
6 rpm	17	6	17	5
3 rpm	14	5	13	4

Table 17

Mud system	PETROFREE LV			
Mud weight, lb/gal	14.0			
Oil/water ratio	70/30			
Contaminant	Drill Solids			
E3, lb/bbl	0		3	
Temperature, °F	40	120	40	120
Plastic viscosity, cP	118	40	115	36
Yield point, lb/100ft ²	38	14	35	14
10 sec gel, lb/100ft ²	16	6	25	6
10 min gel, lb/100ft ²	22	11	30	9
Fann 35 dial readings				
600 rpm	274	94	265	86
300 rpm	156	54	150	50
200 rpm	114	40	110	37
100 rpm	70	25	65	23
6 rpm	17	6	17	5
3 rpm	14	5	13	4

The foregoing description of the invention is intended to be a description of preferred embodiments. Various changes in the details of the described compositions and method can be made without departing from the intended scope of this invention as defined by the appended claims.

We claim:

1. A method of influencing the rheology of a drilling fluid or well service fluid comprising an invert emulsion, said method comprising adding to said fluid at least one non-ionic surfactant, said surfactant being the reaction product of at least one oxide, selected from the group comprising ethylene oxide, propylene oxide and butylene oxide, with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 having structural units of the general formula (I)



where R₁ is a hydrogen atom, or an OH group, or a group OR₂ and where R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):



- and where R₃ is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

2. The method of claim 1 wherein said non-ionic surfactant comprises alkylation products obtained by reacting C₁₂₋₂₂ carboxylic mono-, di- or triglycerides containing structural units of the formula (I) in at least one position 9, 10, 13, or 14 with at least one oxide of the group comprising ethylene oxide, propylene oxide, and butylene oxide.

3. The method of claim 1 wherein said drilling fluid or well service fluid comprises a continuous oil phase that is flowable and pumpable at temperatures
5 at least as low as about 40 degrees Fahrenheit.

4. The method of claim 1 wherein said drilling fluid or well service fluid comprises a continuous oil phase that is flowable and pumpable at temperatures
10 above about 32 degrees Fahrenheit.

5. The method of claim 3 wherein said oil phase comprises compounds or compositions selected from the group comprising:

(a) carboxylic esters of the formula:

15



where R' is a saturated or unsaturated, linear or branched, alkyl radical having about 1 to about 23 carbon atoms and R'' is an alkyl radical, branched or unbranched, saturated or unsaturated, having about 1 to about 23 carbon atoms;

20

(b) linear or branched olefins having about 8 to about 30 carbon atoms;

(c) water-insoluble symmetric or asymmetric ethers of monohydric alcohols of natural or synthetic origin, said alcohols containing about 1 to about 24 carbon atoms;

(d) water-insoluble alcohols of the formula:

25



where R''' is a saturated, unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms; and

(e) carbonic diesters.

30 6. The method of claim 5 wherein said oil phase comprises esters wherein the radical R' is an alkyl radical having about 5 to about 21 carbon atoms.

7. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid in an amount sufficient to effect a reduction in the viscosity of said emulsion.

5 8. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid in an amount sufficient to maintain the flowability and pumpability of said emulsion.

9. The method of claim 1 wherein said surfactant is added to said drilling
10 fluid or well service fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said compound per barrel of said emulsion.

10. The method of claim 1 further comprising adding to said drilling fluid or well service fluid a co-thinner compound having the formula:

15



where R is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about
20 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

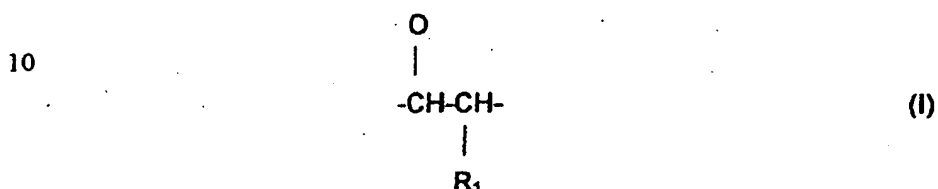
11. The method of claim 10 wherein in said formula for said co-thinner compound, k is zero and m is a number ranging from about 1 to about 10, or m is
25 zero and k is a number ranging from about 1 to about 10.

12. The method of claim 10 wherein in said formula for said co-thinner compound, n is a number ranging from about 1 to about 6, m is a number ranging from about 1 to about 6, and k is zero.

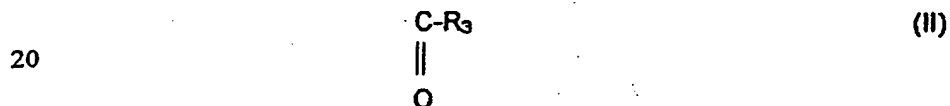
30

13. The method of claim 10 wherein said surfactant and said co-thinner compound are added in proportions ranging from about 1:1 to about 10:1.

14. A drilling fluid or well service fluid comprising a continuous oil phase, water dispersed in said oil phase, solids insoluble in said oil phase, and at least one non-ionic surfactant, said surfactant being the reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C₁₀₋₂₂ carboxylic acids or C₁₀₋₂₂ carboxylic acid derivatives containing at least one double bond in position 9, 10, 13, or 14 having structural units of the general formula (I)



- 15 where R₁ is a hydrogen atom, or an OH group, or a group OR₂, and where R₂ is an alkyl group of about 1 to about 18 carbon atoms, or an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula (II):



where R₃ is a hydrogen atom, or an alkyl group of about 1 to about 21 carbon atoms, or an alkylene group of about 2 to about 21 carbon atoms.

15. The drilling fluid or well service fluid of claim 14 wherein said surfactant is added in sufficient amounts to reduce the viscosity of said fluid.
16. The drilling fluid or well service fluid of claim 14 wherein said surfactant is added to said fluid in quantities ranging from about 0.5 pounds to about 15.0 pounds of said surfactant per barrel of said fluid.
17. The drilling fluid or well service fluid of claim 14 having a yield point of not more than about 75 lbs/100 ft² at about 40°F.

18. The drilling fluid or well service fluid of claim 14 further comprising a compound having the formula:



5

where R'' is a saturated or unsaturated, linear or branched alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10.

10

19. The drilling fluid or well service fluid of claim 18 wherein said surfactant and said compound are in proportions ranging from about 1:1 to about 10:1.

20. The method of claim 1 wherein said surfactant is added to said drilling fluid or well service fluid during preparation of said fluid or after such fluid has begun service in the wellbore.

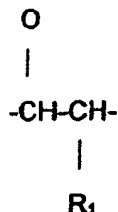
21. The method of claim 10 wherein said co-thinner compound is added to said fluid during preparation of said fluid or after said fluid has begun service in the wellbore.

Abstract

A method of reducing the viscosity of invert emulsions and oil-based drilling fluids and well service fluids comprising such emulsions over a broad temperature range is disclosed. The method comprises adding to said invert emulsions of the invention a non-ionic surfactant alone or in combination with a co-thinner having the formula:



where R'' is a saturated or unsaturated, linear or branched, alkyl radical having about 8 to about 24 carbon atoms, n is a number ranging from about 1 to about 10, m is a number ranging from about 0 to about 10, and k is a number ranging from about 0 to about 10. The non-ionic surfactant is a reaction product of ethylene oxide, propylene oxide and/or butylene oxide with C_{10-22} carboxylic acids or C_{10-22} carboxylic acid derivatives containing at least in position 9/10 and/or 13/14 structural units of the general formula:



where R_1 is a hydrogen atom or an OH group or a group OR_2 . R_2 is an alkyl group of about 1 to about 18 carbon atoms, an alkenyl group of about 2 to about 18 carbon atoms, or a group of the formula:



R_3 is a hydrogen atom, an alkyl group of about 1 to about 21 carbon atoms or an alkylene group of 2 to 21 carbon atoms.

TABLE 3. INTOIL™ 100% OIL FORMULATIONS USING MINERAL OIL, DENSITY : 12 ppG				
ADDITIVES	F2	F10	F11	F12
MINERAL OIL (bbls)	0.817	0.817	0.817	0.817
POLYMERIC ADDITIVE (ppb)	3	4	3	4
ORGANOPHILIC BENTONITE (ppb)	12	10	12	10
EMULSIFIER (ppb)	6	6	—	—
WETTING AGENT (ppb)	—	—	6	6
LIME (ppb)	10	10	10	10
CALCIUM CARBONATE (ppb)	—	—	—	—
BARITE (ppb)	272	272	272	272
AGING TEMPERATURE (°F), 16 HRS	300	300	300	300
PLASTIC VISCOSITY (cP) @ 150 °F	38/21	32/28	25/48	25/43
YIELD POINT (lb/100 ft ²)	21/19	15/24	18/36	13/29
L6 (lb/100 ft ²)	11/8	8/6	7/12	6/9
L3 (lb/100 ft ²)	10/7	7/5	6/10	5/7
GEL 10" (lb/100 ft ²)	9/7	7/6	6/10	5/8
GEL 10' (lb/100 ft ²)	11/12	8/10	7/14	6/10
HPHT FILTRATE VOLUME AT 300 °F, AFTER AGING (ml/30 min)	2.0	3.0	4.0	3.0

TABLE 4. INTOIL™ 100% OIL FORMULATIONS USING MINERAL OIL , 15 ppG, WITH DIFFERENT WEIGHTING AGENTS			
ADDITIVES	F13	F14	F15
MINERAL OIL (bbls)	0.714	0.762	0.762
POLYMERIC ADDITIVE (ppb)	4	4	4
ORGANOPHILIC BENTONITE (ppb)	8	8	10
EMULSIFIER (ppb)	6	6	6
LIME (ppb)	2	2	2
BARITE (ppb)	425	—	—
HEMATITE (ppb)	—	415	415
AGING TEMPERATURE (°F), 16 HRS	350	350	350
PLASTIC VISCOSITY (cP) @ 150 °F	45/48	33/22	38/51
YIELD POINT (lb/100 ft ²)	20/31	9/16	9/25
L6 (lb/100 ft ²)	9/11	3/4	3/7
L3 (lb/100 ft ²)	8/9	3/3	3/6
GEL 10" (lb/100 ft ²)	8/9	3/5	3/6
GEL 10' (lb/100 ft ²)	9/11	4/9	3/8
HPHT FILTRATE VOLUME AT 350 °F, AFTER AGING (ml/30 min)	3.0	3.0	3.0

TABLE 5. INTOIL™ 100% OIL FORMULATIONS USING MINERAL OIL, BARITE AS WEIGHTING AGENT AND EMULSIFIER OR WETTING AGENT, 15 ppg

<u>ADDITIVES</u>	<u>F13</u>	<u>F16</u>
MINERAL OIL (bbls)	0.714	0.714
POLYMERIC ADDITIVE (ppb)	4	3
ORGANOPHILIC BENTONITE (ppb)	8	6
EMULSIFIER (ppb)	6	—
WETTING AGENT (ppb)	—	6
LIME (ppb)	2	4
BARITE (ppb)	425	425
AGING TEMPERATURE (°F), 16 HRS	350	350
PLASTIC VISCOSITY (cP) @ 150 °F	45/48	28/36
YIELD POINT (lb/100 ft ²)	20/31	9/11
L6 (lb/100 ft ²)	9/11	5/5
L3 (lb/100 ft ²)	8/9	4/4
GEL 10" (lb/100 ft ²)	8/9	4/4
GEL 10' (lb/100 ft ²)	9/11	5/6
HPHT FILTRATE VOLUME AT 350 °F, AFTER AGING (ml/30 min)	3.0	4.0

TABLE 6. INTOIL™ 100% OIL FORMULATIONS USING MINERAL OIL, BARITE OR HEMATITE AND EMULSIFIER OR WETTING AGENT, 15 ppg

<u>ADDITIVES</u>	<u>F13</u>	<u>F15</u>	<u>F17</u>	<u>F18</u>
MINERAL OIL (bbls)	0.714	0.763	0.763	0.763
POLYMERIC ADDITIVE (ppb)	4	4	4	3
ORGANOPHILIC BENTONITE (ppb)	8	10	8	6
EMULSIFIER (ppb)	6	6	—	—
WETTING AGENT (ppb)	—	—	6	6
LIME (ppb)	2	2	2	4
BARITE (ppb)	425	—	—	—
HEMATITE (ppb)	—	415	415	415
AGING TEMPERATURE (°F), 16 HRS	350	350	350	350
PLASTIC VISCOSITY (cP) @ 150 °F	33/22	38/51	43/50	23/28
YIELD POINT (lb/100 ft ²)	9/16	9/25	13/26	13/10
L6 (lb/100 ft ²)	3/4	3/7	4/7	5/5
L3 (lb/100 ft ²)	3/3	3/6	3/5	4/4
GEL 10" (lb/100 ft ²)	3/5	3/6	4/5	4/4
GEL 10' (lb/100 ft ²)	4/9	3/8	6/15	4/5
HPHT FILTRATE VOLUME AT 350 °F, AFTER AGING (ml/30 min)	3.0	3.0	3.0	2.0

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TABLE 7. INTOIL™ 100% OIL FORMULATIONS USING MINERAL OIL WITH EMULSIFIER AND ORGANOPHILIC HECTORITE, 18 ppb

ADDITIVES	F18	F19	F20
MINERAL OIL (bbls)	0.68	0.68	0.68
POLYMERIC ADDITIVE (ppb)	3.5	3.5	3.5
ORGANOPHILIC HECTORITE (ppb)	6	6	6
EMULSIFIER (ppb)	6	6	6
LIME (ppb)	2	3	4
HEMATITE (ppb)	561	561	561
AGING TEMPERATURE (°F), 16 HRS	400	400	400
PLASTIC VISCOSITY (cP) @ 150 °F	54/55	50/52	55/52
YIELD POINT (lb/100 ft ²)	23/42	20/24	30/34
L6 (lb/100 ft ²)	10/22	8/9	10/20
L3 (lb/100 ft ²)	10/23	7/8	8/17
GEL 10" (lb/100 ft ²)	8/21	7/8	9/18
GEL 10' (lb/100 ft ²)	11/23	11/12	11/25
HPHT FILTRATE VOLUME AT 400 °F, AFTER AGING (ml/30 min)	5.0	4.0	4.0

TABLE 8. INTOIL™ 100% OIL FORMULATION USING MINERAL OIL, WITH ORGANOPHILIC BENTONITE AND WETTING AGENT, 18 ppb

ADDITIVES	F21
MINERAL OIL (bbls)	0.68
POLYMERIC ADDITIVE (ppb)	3.5
ORGANOPHILIC BENTONITE (ppb)	6
WETTING AGENT (ppb)	6
LIME (ppb)	4
HEMATITE (ppb)	561
AGING TEMPERATURE (°F), 16 HRS	400
PLASTIC VISCOSITY (cP) @ 150 °F	32/59
YIELD POINT (lb/100 ft ²)	11/28
L6 (lb/100 ft ²)	6/8
L3 (lb/100 ft ²)	5/6
GEL 10" (lb/100 ft ²)	5/6
GEL 10' (lb/100 ft ²)	7/10
HPHT FILTRATE VOLUME (ml/30 min) AT 400 °F, AFTER AGING	8.0

TABLE 9. STANDARD FORMULATION FOR THE INVERT EMULSION INTOIL™ DRILLING FLUID		
ADDITIVE	FUNCTION	CONCENTRATION
GASOIL OR MINERAL OIL (% V/V)	CONTINUOUS PHASE	80 - 60
EMULSIFIER	EMULSIFIER/WETTING AGENT	10 ppb
POLYMERIC ADDITIVE	HPHT FLUID LOSS CONTROL AGENT	2 - 6 ppb
WATER (% V/V)	DISCONTINUOUS PHASE	20 - 40
CALCIUM CHLORIDE	BRINE SOURCE	290,000 ppm
LIME	ALKALINITY AGENT	4 ppb
WEIGHTING AGENT	HOLE STABILITY	AS NEEDED

TABLE 10. INTOIL™ INVERT EMULSION FORMULATION USING MINERAL OIL AND DIFFERENT CONCENTRATIONS OF EMULSIFIER, DENSITIES: 9, 15 AND 18 ppb								
ADDITIVES	F22	F23	F24	F25	F26			
DENSITY (ppg)	9	15	15	15	18			
MINERAL OIL (bbls)	0.663	0.503	0.503	0.503	0.504			
POLYMERIC ADDITIVE (ppb)	6	3	3	3	2.5			
EMULSIFIER (ppb)	10	10	8	6	10			
WATER/CALCIUM CHLORIDE (bbls/ppb)*	0.284/ 46.33	0.216/28.3	0.216/28.3	0.216/28.3	0.126/16.6			
LIME (ppb)	6	6	6	6	6			
CALCIUM CARBONATE (ppb)	51.61	—	—	—	—			
BARITE (ppb)	—	377.56	377.56	377.56	526.7			
AGING TEMPERATURE (°F), 16 HRS	300	300	350	300	350	300	350	300
PLASTIC VISCOSITY (cP) @ 150 °F	35/30	35/47	42/46	39/42	39/47	38/44	39/44	50/45
YIELD POINT (lb/100 ft²)	10/15	21/12	24/7	21/13	20/9	19/13	18/10	18/20
L6 (lb/100 ft²)	7/6	9/8	12/6	12/8	9/7	10/8	10/6	9/10
L3 (lb/100 ft²)	6/5	8/7	10/5	11/7	9/7	9/7	9/5	7/9
GEL 10" (lb/100 ft²)	5/5	8/7	10/5	11/7	10/7	9/7	9/5	8/9
GEL 10' (lb/100 ft²)	7/7	9/9	11/6	11/9	9/6	10/8	10/6	7/11
HPHT FILTRATE VOLUME AT AGING TEMPERATURE, AFTER AGING (ml/30 min)	1.4	2.0	2.0	2.0	2.0	2.0	3.0	3.8

* Note : calcium chloride is predissolved in water

TABLE 11. INITIAL FORMULATION OF 100% OIL INTOIL™ DRILLING FLUID USED IN WELL COPORO-12

<u>ADDITIVES</u>	<u>CONCENTRATION</u> (ppb)
MINERAL OIL	—
ORGANOPHILIC HECTORITE	5.0
POLYMERIC ADDITIVE	2.5
WETTING AGENT	3.0
RHEOLOGY MODIFIER	2.0
LIME	2.0
CALCIUM CARBONATE	132

TABLE 12. INITIAL PROPERTIES OF THE FORMULATION OF 100 % OIL INTOIL™ DRILLING FLUID USED IN WELL COPORO-12

<u>PROPERTY</u>	<u>VALUE</u>
O/W RATIO (% V/V)	100
DENSITY (ppg)	9.0
FUNNEL VISCOSITY (s/qt)	120
PLASTIC VISCOSITY (cP) @ 150 °F	22
YIELD POINT (lb/100 ft²)	16
GEL 10"/10' (lb/100 ft²)	7/11
L6/L3 (lb/100 ft²)	7/6
PoM	0.075
HPHT FILTRATE VOLUME AT 220°F (ml/30 min)	6.2
MUD CAKE THICKNESS (inches)	1/32
SOLIDS (% V/V)	12

TABLE 13. AVERAGE PROPERTIES OF 100 % OIL INTOIL™ DRILLING FLUID USED IN WELL COPORO-12

<u>PROPERTY</u>	<u>VALUE</u>
O/W RATIO (% V/V)	100
DENSITY (ppg)	9.0-10.3
FUNNEL VISCOSITY (s/qt)	80-97
PLASTIC VISCOSITY (cP) @ 150 °F	24-40
YIELD POINT (lb/100 ft²)	9-20
GEL 10"/10' (lb/100 ft²)	7/11-17/28
L6/L3 (lb/100 ft²)	7/10-6/9
PoM	0.20-0.45
HPHT FILTRATE VOLUME AT 220 °F (ml/30 min)	5.0-10.0
MUD CAKE THICKNESS (in.)	1/32
PPT SPURT (ml)	2
PPT TOTAL (ml)	10
SAND CONTENT (% V/V)	1/4
SOLIDS CONTENT (% P/P)	12-25

TABLE 14. PROPERTIES OF INTOIL™ FLUID USED IN WELL COPORO-12, AS A FUNCTION OF DEPTH

DAY	DEPTH (ft)	DENSITY (ppg)	FUNNEL VISC. (cgu)	PV (cp)	YP (lb/100ft ²)	L6 (lb/100ft ²)	L3 (lb/100ft ²)	Gel 10" (lb/100ft ²)	Gel 10" (lb/100ft ²)	HPHT FILTR. VOL. @ 220 °F (ml/30 min)	SOLIDS CONT. (% V/V)	OIL CONT. (% V/V)	WATER CONT. (% V/V)	ELECTR. STAB. (V)
1	612	9.0	—	30	20	7	6	7	18	—	12	88	—	1,600
2	910	9.0	95	26	10	8	7	8	20	6.8	12	88	—	2,000
3	2,230	9.1	90	26	13	8	7	7	20	6.8	12	88	—	2,000
4	2,957	9.3	90	25	12	8	7	7	20	6.4	13	87	—	2,000
5	2,992	9.3	90	20	9	7	6	6	17	7.4	12	86	2	1,500
6	2,992	9.6	95	30	16	8	7	6	20	10.0	10	76	14	1,100
7	3,490	9.8	80	28	14	9	8	7	20	10.0	16	76	8	1,500
8	4,279	10.1	89	28	13	10	9	10	22	8.0	22	72	6	1,350
9	4,438	10.3	91	30	14	9	8	10	28	7.8	22	71	6	1,300
10	4,870	10.4	92	33	15	10	9	12	27	5.8	23	73	4	1,300
11	5,560	10.4	90	37	15	10	9	12	28	5.2	23	73	3	1,300
12	6,450	10.4	90	37	16	10	9	13	28	5.0	24	73	2	1,400
13	6,707	10.4	90	35	12	9	8	11	25	5.2	25	73	2	1,400
14	6,707	10.4	95	35	12	9	8	13	26	5.2	25	73	2	1,400
15	6,951	10.4	88	37	13	9	8	13	26	5.4	25	73	2	1,400
16	6,960	10.4	94	40	14	10	9	13	26	5.6	25	73	2	1,400
17	6,960	10.4	97	40	15	10	9	13	27	5.6	25	73	2	1,450
18	6,960	10.4	90	40	15	10	9	14	27	5.6	25	73	2	1,500
19	6,960	10.4	84	39	13	9	8	11	24	5.6	25	73	2	1,500
20	6,960	10.4	90	39	13	9	8	11	25	5.6	25	73	2	1,500
21	6,960	10.4	92	39	13	9	8	11	25	5.6	25	73	2	1,500

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